

Surface and Microanalysis Science Division - Table of Contents

Division Overview	2
Development of Accurate Quantitative Analysis Procedures for High-Angle X-Ray Emission Spectroscopy	12
Effects of Backscattered Electrons on the Lateral Resolution and Analysis Area of a Scanning Auger Microscope	15
Images of Particle-Like Fractals with Differing Shapes and Boundary Fractal Dimensions for Testing Algorithms that Measure Fractal Dimension	18
Preliminary Evaluation of Positive Secondary Ion Yield Enhancements Using Chlorodifluoromethane and Tetrachloroethene Backfilling	20
Precision Isotopic Measurements with the NIST High Performance Secondary Ion Mass Spectrometry Facility	22
Verification of Calibration Procedure for Testing Military Gas Masks	24
Characterization of Trace Explosive Detection Equipment for Airport Security Applications	26
Results of SiO ₂ /Si Comparison between Neutron Scattering and GIXPS	29
Mass Determination From Particle Size and Number	31
XML for Microanalysis	33
Development of SiGe Compositional Standards for the Semiconductor Industry	35
High Speed Elemental Mapping with the Silicon Drift X-ray Detector (SDD) on an SEM	37
NIST Microcalorimeter Detector for High Resolution X-ray Detection	39
Localization of Boron Neutron Capture Chemotherapeutic Agents by Secondary Ion Mass Spectrometry	41
New Version of the NIST Electron Elastic-Scattering Cross-Section Database	43
Chemical Imaging of Polymer Blends with Confocal Raman Microscopy	45
Spectroscopic Study of the Structure of Oligo-phenylene-ethynylene Monolayers with Molecular Electronics Implications	48
Electronic Structure and Transport in Model Molecular Electronic Systems	50
Fabrication of the Building Blocks of Multifunctional Nanoscale Sensors	52
Quantum Mirages in STM of Surface Nanostructures	54
Total Carbon Determination In Buffalo River Sediment Using Isotope Dilution Mass Spectrometry	56
Gravimetric Results of a Fine Particulate Carbonaceous Reference Material on Quartz-Fiber Filter (SRM Project 2784)	58
Chemometric optimization of thermal-optical analysis in determining black carbon in atmospheric PM _{2.5}	60
Characterization of the Morphology of Faceted Nanoparticles by Transmission Electron Microscopy	62
Bevel Craters For Surface Analysis Of AlGaAs/GaAs Multi-layer Structures	64
Autoradiography Measurements to Quantity Activity of Co-60 Particles	66
The NIST-EPA Interagency Agreement to Develop Metrology Supporting PM _{2.5} Research: Status and Completion of Selected Tasks	68

SURFACE AND MICROANALYSIS SCIENCE DIVISION

Mission:

As part of the Chemical Science and Technology Laboratory at NIST the Surface and Microanalysis Science Division serves as the Nation's Reference Laboratory for chemical metrology research, standards, and data to:

- Characterize the spatial and temporal distribution of chemical species; and
- Improve the accuracy, precision, sensitivity, selectivity, and applicability of surface, microanalysis, and advanced isotope measurement techniques.

The Division provides the tools for the Nation's measurement communities to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and improve public health, safety, environmental quality, and national security. We perform research to:

1. Determine the chemistry and physics of surfaces, interfaces, particles, and bulk materials, and their interactions with a broad spectrum of analytical probes including electrons, photons, ions, atoms, and molecules;
2. Determine the chemical and isotopic compositions, morphology, crystallography, and electronic structure at scales ranging from millimeters to nanometers;
3. Determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid surfaces and interfaces as well as within materials and devices;
4. Study the total chemical measurement process as well as source apportionment in atmospheric chemistry using advanced isotope metrology and chemometrics; and
5. Develop and certify key Standard Reference Materials and Standard Reference Data.

Organizational Structure:

The Division is organized into four groups that serve as the foci of technical expertise and research contributing to seven Division-wide project areas and impacting a variety of CSTL programs. The Division also benefits from the presence of two NIST Fellows who, although not associated with specific groups, interact extensively with a broad cross section of the Division and with organizations internal and external to NIST.

Atmospheric Chemistry Group

- Develops and applies methods for the concentration, separation, and isotope measurement of trace atmospheric gases and particles.
- Investigates chemometric methods in applied analytical problems involving multivariate and multicomponent systems.
- Develops theoretical, experimental, and mathematical methods for apportioning natural and anthropogenic sources of carbonaceous gases and particles.
- Performs isotope measurement: accelerator mass spectrometry for ^{14}C , and high precision mass spectrometry for ^{13}C .

Microanalysis Research Group

- Performs research, development, and applications on microbeam analysis techniques for the chemical, morphological, and crystallographic characterization of matter down to the nanometer length scale.
- Advances analytical techniques that primarily utilize excitation beams of electrons and X-rays to generate a signal that yields elemental and molecular information.
- Develops improved methods of quantification and analytical modeling as well as Standard Reference Materials and Data for a wide variety of industry applications that use:
 - Scanning electron microscopy
 - Electron probe microanalysis
 - Analytical electron microscopy
 - Scanning Auger microprobe
 - Micro X-ray fluorescence
 - X-ray Photoelectron Spectroscopy

Analytical Microscopy Group

- Conducts research on the chemical and structural properties of matter by applying various ion and photon based microscopies whose resolution range from micrometers to nanometers.
- Researches the fundamental aspects of the excitation process, quantification, standards development, instrumental improvements, and data analysis challenges associated with these analytical methods.
- Conducts research on autoradiography and nuclear track methods.
- Conducts research in generation and size-calibration of particles.
- Applies analytical microscopy methods to problems in materials science, semiconductor technology, biotechnology, and environmental science that use:
 - Secondary ion mass spectrometry by
 - Ion microscopy
 - Time-of-flight
 - Laser Raman microprobe
 - Fourier-transform infrared microprobe
 - Optical microscopy
 - X-ray diffraction

Surface and Interface Research Group

- Conducts theoretical and experimental research concerning chemical processes at surfaces and interfaces.
- Develops and applies surface sensitive diagnostics involving lasers and proximal probes with fine spatial and spectral resolution.

- Characterizes mechanisms of energy transfer, structures of complex interfaces, and the chemical reactivity of solid-solid, solid-liquid, and solid-vacuum interfaces
- Performs calculations to investigate the interactions of atoms, molecules, electrons, and radiation with surfaces and interfaces.
- Applies advanced measurement methods to critical problems in semiconductor, polymer, biomolecular, catalytic, electronic, and nanoscale science, including:
 - Non-linear optical and photoelectron spectroscopies
 - Far-Field chemical imaging microscopies
 - Near-Field optical and microwave nanoscale probes
 - Atomic force and conductive scanned probe microscopies

With the beginning of fiscal year 2003, the Division will transition to a structure built on three groups, rather than four. Much of the light atom mass spectrometry expertise in the Atmospheric Chemistry Group will be merging with the Analytical Microscopy Group; Raman expertise within the Division will be centralized in the Surface and Interface Research Group, while the data and informatics strengths of the Division will be anchored in the Microanalysis Research Group. This realignment of technical expertise is expected to lead to improved application of Division strengths to priority Division Projects.

Technical Projects Within The Division

The major activities of the Division align primarily with four of CSTL's industry-focused Programs: *Microelectronics, Forensics and HLS, Industrial and Analytical Instruments and Services*, and *Environmental Technologies and Services*. In addition, the Division undertakes a range of activities that address *Technologies for Future Measurements and Standards*. The Division also plays a significant but smaller role in other CSTL Programs, such as *International Measurement Standards, Automotive and Aerospace, and Pharmaceuticals and Biomanufacturing*. Technical activities within the Division are organized under seven Division Projects in order to realize cross-Program benefits derived from infrastructural aspects of our core technical strengths. The mapping from each Division Project to specific CSTL Program is provided below.

Spatially Resolved Chemical Characterization of Optoelectronic and Semiconductor Systems. Electronic and advanced materials are increasingly impacted by compositional changes on the submicrometer length scale. This is routinely seen in the semiconductor area where the ever-shrinking size of device features continues to allow the industry to realize Moore's Law – the exponential increase in transistor density on a chip. Current Division efforts span thin-film characterization, surface chemical growth mechanisms, and novel nanostructures for the electronics industry. The focus on microelectronics can be seen in the activities of this program, with increased efforts being directed toward the development of measurement techniques that address needs which range from those of the International SEMATECH as seen in their International Technology Roadmap for Semiconductors to the determination of contaminants in starting materials and finished products. Activities this year span silicon-germanium compositional standards, SiO₂

thickness measurements, and improved SIMS methods for depth profiling characterization.

These activities support the CSTL *Microelectronics* Program:

- “Development of SiGe Compositional Standards for the Semiconductor Industry” R.B. Marinenko, J.T. Armstrong, S. Turner, E.B. Steel, and D.S. Simons
- “Results of SiO₂/Si Comparison between Neutron Scattering and GIXPS” T. Jach and E. Landree (Guest Worker) (*Industrial and Analytical Instruments and Services*)
- “Preliminary Evaluation of Positive Secondary Ion Yield Enhancements Using Chlorodifluoromethane and Tetrachloroethene Backfilling” P.H. Chi and J.G. Gillen (*Industrial and Analytical Instruments and Services*)
- “Development and Certification of SRM 2133 - Phosphorus Implant in Silicon for SIMS Calibration” D.S. Simons (837) and R.L. Paul (839)

Advanced Probes for Nano-Scale Chemical Characterization. The emergence of Nanotechnology, with its associated measurement challenges, carries significant implications for many of the Division technical activities. The need for improved spatial resolution currently limits the ability of Industry to answer key questions regarding the chemical composition of surfaces and interfaces. Needs range from improved chemical and structural diagnostics to phase identification and trace compositional analysis. In addition to meeting current industry needs in these areas, there is a continuing demand for new measurement methods to be developed that will be positioned to meet emerging measurement challenges. The Division develops measurement tools that enable the chemical characterization (elements, isotopes, and molecules) at millimeter to nanometer spatial scales with major, minor, and trace concentrations. We strive to develop measurement tools such that the ‘microspatial’ relationships of chemical species can be correlated with specific macroscopic properties.

Improvements in mass resolution without loss in throughput are being pursued in Secondary Ion Mass Spectrometry to broaden the impact of this technique to include systems previously hampered by isotopic interferences, with applications ranging from semiconductor technology and medical treatments. Innovative scanned probe methods are being developed to combine optical contrast mechanisms with near-field measurements to characterize electronic materials, drug delivery systems, and advanced materials on the nanoscale. The Division continues to push the measurement envelope for nanoscale characterization in TEM methods, radionucleotides, and sensors through the development of collaborative efforts with MSEL, BRFL, PL and other Divisions within CSTL. While directly tied to the CSTL efforts in *Technologies for Future Measurements & Standards*, the connection to other CSTL programs is quite apparent.

- “Autoradiography Measurements to Quantify Activity of Co-60 Particles” C.J. Zeissler and R.M. Lindstrom (839) (*Environmental Technologies and Services*)

- “Characterization of the Morphology of Faceted Nanoparticles by Transmission Electron Microscopy” S. Turner and D.S. Bright. (*Industrial and Analytical Instruments and Services*)
- “Quantum Mirages in STM of Surface Nanostructures” J.W. Gadzuk
- “Fabrication of the Building Blocks of Multifunctional Nanoscale Sensors” R.M. Hernández and S.J. Stranick (*Biomaterials*)
- “Precision Isotopic Measurements with the NIST High Performance Secondary Ion Mass Spectrometer Facility” A.J. Fahey (*Microelectronics*)
- “Localization of Boron Neutron Capture Chemotherapeutic Agents by Secondary Ion Mass Spectrometry” S.V. Roberson and J.G. Gillen (*Healthcare and Medical Products/Services*)

Molecular Electronics. The continued shrinking of electronic devices points to the need for entirely new technologies to meet the performance requirements anticipated for computers in the year 2020. Electronic components that incorporate molecular species to realize the circuit function are being looked to as a promising solution. The Division is involved in a Competence Project with Divisions 836 and 838 in CSTL and Division 812 in the Electronics and Electrical Engineering Laboratory to develop measurement methods appropriate to these nanoscale materials. Due to the challenges that must be overcome in the field of Molecular electronics, this project is part of the CSTL efforts in *Technologies for Future Measurements & Standards*.

- “Electronic Structure and Transport in Model Molecular Electronic Systems” J.D. Batteas, S.W. Robey (837), R.D. van Zee, C.D. Zangmeister (836) (*Microelectronics*)
- “Spectroscopic Study of the Structure of Oligo-phenylene-ethynylene Monolayers with Molecular Electronic Implications” C.S.-C. Yang, P.T. Wilson, L.J. Richter (837), R.D. van Zee (836), J.J. Stapleton, D.L. Allara (Pennsylvania State University) (*Microelectronics*)

Many of the Division efforts span challenges in measurement science associated with the chemical characterization of materials. These may be in the area of small particles, reactions of surface layers of atomic dimension, or minor isotopics that are found in environmental samples. To sustain our position in credible measurements in such vanishingly small samples, the Division invests resources in a range of efforts to provide appropriate quality control and quality assurance capabilities of interest to U.S. industry. Our efforts aid industry in achieving ISO 9000 certification requirements, and provide the basis for traceability among the national and international standards bodies, industries and governments.

Chemical Characterization: Powders and Particulate Matter. Particle measurement issues play a prominent role in this program as they arise in industrial, environmental, and processing environments. A key focus of the Division is to provide appropriate measurement tools for different particle analysis. Within this program, we direct our efforts to identify samples, contaminants, or analyze particles in advanced materials. Particular attention is given to the characterization of individual particles and to populations of particles. To this end, automated particle measurement methods are

utilized, and software packages are developed or extended for data collection, visualization, and interpretation. Standards, data and measurement protocols are developed to support quality assurance efforts. Many of the measurement capabilities that we develop within this project are transferred to other government agencies such as DoD, DoE, EPA and IAEA.

- “Chemometric Optimization of Thermal-optical analysis in determining black carbon in atmospheric PM_{2.5}” J.M. Conny, D.B. Klinedinst, S.A. Wight (837), J.L. Paulsen (839) (*Environmental Technologies and Services*)
- “Gravimetric results of a fine particulate carbonaceous reference material on quartz-fiber filter (SRM Project 2784)” G.A. Klouda (837) and J.J. Filliben (898) (*Environmental Technologies and Services*)
- “Verification of Calibration Procedure for Testing Military Gas Masks” R.A. Fletcher, R.L. King, J.A. Small (837), M.R. Winchester (839), J.C. Yang and G.W. Mulholland (866) (*Forensics and HLS*)
- “Images of Particle-like Fractals with Differing Shapes and Boundary Fractal Dimensions for Testing Algorithms that Measure Fractal Dimension” D.S. Bright. (*Industrial and Analytical Instruments and Services*)
- “Characterization of Trace Explosive Detection Equipment for Airport Security Applications” J.G. Gillen, R.A. Fletcher, S.A. Wight, S.V. Roberson, E.S. Etz, A.P. Lindstrom, C.J. Zeissler, J.R. Verkouteren (837), B.A. Benner (839), and R. Lareau (TSA) (*Forensics and HLS*)

Chemical Characterization of Materials: Surfaces and Interfaces. Characterization of surfaces and interfaces demands methods that can address the chemical and structural changes that occur in different environments. Surface reactions are central in the area of catalysis, solid-state sensors, adsorption, and electronic device fabrication. The Division provides measurement tools, fundamental data, and models that address the events that occur at surface and interfaces during basic chemical reactions. These efforts are part of the CSTL *Industrial and Analytical Instruments and Services* Program. Efforts this year have led to:

- “Bevel Craters for Surface Analysis of AlGaAs/GaAs Multi-layer Structures” S.A. Wight, J.G. Gillen, and A.J. Fahey (*Microelectronics*)
- “Chemical Imaging of Polymer Blends with Confocal Raman Microscopy” C.A. Michaels. (*Chemical and Allied Products*)
- “Effects of Backscattered Electrons on the Lateral Resolution and Analysis Area of a Scanning Auger Microscope” C.J. Powell, S.A. Wight, and J.T. Armstrong
- “New Version of the NIST Electron Elastic-Scattering Cross-Section Database” C.J. Powell, A. Jablonski (Contractor), and F. Salvat (Univ. of Barcelona)

Analytical Tools for High-Throughput Experimentation in Materials and Chemical Manufacturing. The emergence of high throughput methods in materials discovery and process optimization is causing industry to re-assess many of the methods that have traditionally been used in their laboratories. Utilization of smaller samples, continuous gradient libraries, advanced design-of-experiment approaches, new data mining tools, and

performance-based screening tools, is demanding new approaches to quality control, standards, and data exchange protocols. Division efforts involved with advanced detector technologies to allow existing electron microscopies to process samples at a speed commensurate with high-throughput methods, data transfer protocols to allow data from a range of instruments to be stored and evaluated using common methods, and performance-based probes. Many of the Division efforts are aligned with the needs of the CSTL *Industrial and Analytical Instruments and Services* Program.

- “XML for Microanalysis” J.H.J. Scott
- “NIST Microcalorimeter Detector for High Resolution X-ray Detection” J.A. Small, D.E. Newbury, R.L. King, T. Jach (837), S.W. Nam, K.D. Irwin, and S. Deiker (814) (*Environmental Technologies and Services*)
- “Development of Accurate Quantitative Analysis Procedures for High-Angle X-ray Emission Spectroscopy” J.T. Armstrong and J.A. Small.
- “High Speed Elemental Mapping with the Silicon Drift X-ray Detector (SDD) on an SEM” D.E. Newbury, J.A. Small, and D.S. Bright. (*Microelectronics*)

Environmental Chemical Metrology. Microscale analysis also plays a critical role in measurements associated with environmental issues. From the submicrometer fibers that are found in asbestos, to the analysis of trace isotopic species that can be indicative of global-scale climate change trends, the ability to analyze on the micrometer and submicrometer length scale is essential. Division efforts in this area find close support in some of the particle analysis efforts that address atmospheric particles such as those in the PM_{2.5} activities. These activities support the CSTL *Environmental Technologies and Services* Program:

- “Total Carbon Determination in Buffalo River Sediment Using Isotope Dilution Mass Spectrometry: Comparison of Techniques” D.B. Klinedinst, R.M. Verkouteren (837), and K. Revesz (USGS)
- “Mass Determination from Particle Size and Number” J.R. Verkouteren (837) and A.G. Wylie (Univ. of Maryland)

Needs Assessment:

The Division benefits from input as it prioritizes its technical activities. One key source of information is feedback and input derived from technical meetings and workshops. In 2002, the Division organized, supported, and/or led an increased number of these feedback opportunities, exploring and exploiting new avenues to provided increased clarity and detail for the direction of our activities. Highlights from 2002 include:

- **Ninth Topical Conference on Quantitative Surface Analysis**, Morgan Hill, CA, October, 2001. The Conference focused on measurement issues of concern to the Microelectronics Community and provided detailed insights into measurement challenges for that industry.
- **International Workshop on X-Ray Photoelectron Spectroscopy: From Spectra to Results – Towards an Expert System**, St. Malo, France, April, 2002.

This international meeting served as a forum for exploring the standards needs for fully automated surface analysis systems.

- **Near-Field Optics 7 – Near-Field Optics and Related Techniques**, Rochester, NY, August 2002. This biennial meeting provided a sampling of international opinion on measurement standards needs for this rapidly growing field of microanalysis.
- NIST – Micro Analysis Society Topical Workshop **Understanding the Accuracy Barrier of Quantitative Electron Beam X-Ray Microanalysis and the Role of Standards**, Gaithersburg, MD, April, 2002. Approximately 100 participants measurement challenges, approaches and needs. Well over half of the participants in this workshop were from industry. Increased access to the meeting was enabled by WEB casting the meeting. This was our first use of distance participation in such a workshop, and proved to be quite effective in expanding the scope of participants. The content of this workshop will be made even more widely available with publication in 2003 of the workshop proceeding.
- **NIST Day**, Austin, TX, July 2002. NIST scientist and engineers met with the semiconductor industry in Austin to develop closer working ties and help each other understand industry needs and matching NIST capabilities.
- American Vacuum Society Topical Conference **Understanding and Operating in Threat Environments**, Monterey, CA, May 2002. This timely workshop provided a valuable opportunity to address current scientific and technical issues in detection, protection, and decontamination technologies that are associated with threats of all sources. This open forum provided a valuable opportunity for discussion of measurement and standards issues that are anticipated in this emerging area of concern.
- **Orthopedic Surgical Manufacturers Association**, Plymouth, MA, July 2002. A discussion of surface and particulate contamination characterization needs was held with this association of 30n orthopedic implant manufacturers.
- **Homeland Security**. Met with technical representatives from TSA, FBI, USSS, ATF, and DoD to discuss microanalysis standards needs related to Homeland Security.

Facilities:

Fiscal year 2002 marked several advances in measurement capabilities for the Division. A new SIMS instrument was added to the existing suite of sector and time-of-flight instruments. The new instrument, a Cameca ims-1270, is one of only three such instruments in the United States. The capability of operating at increased mass resolution without sacrificing throughput is seen to be critical for address questions spanning semiconductor contamination to drug delivery efficiency.

The Division has acquired (either through purchase or loan) three instruments designed for trace explosives detection. These instruments, in conjunction with existing SIMS, ESEM, and Raman facilities, are providing critical resources for our activities with TSA to understand and provide standards for explosive detection portals.

Two infrared microscopes were also acquired by the Division. These facilities will complement the near-field facilities within the Division, and will provide the Division with the ability to bring its infrared expertise to spectral imaging measurement challenges.

Several capital equipment purchases in support of NIST competence projects were completed in FY2002. A variable temperature UHV AFM/STM was purchased to provide state-of-the-art instrumentation to probe the electron transport properties of isolated molecules and nanoscale aggregates of "MolE" molecules. Also, an ultrafast laser with harmonic generation to cover the near-IR to the UV was acquired as part of the multispectral probe development for high throughput experimentation.

Planning for relocation of the majority of the Division facilities in the Advanced Measurements Laboratory continued in 2002. Office assignments, final laboratory services and laboratory locations, and preliminary migration plans have been developed in preparation for building occupancy in FY2004.

Staff Recognition:

Lee Richter received the **U.S. Department of Commerce Bronze Medal** for his scientific insights and creativity in the development and application of nonlinear optical spectroscopies for critical problems in surface analysis. Non linear spectroscopy is uniquely interface specific and can provide unprecedented detail with respect to interface structure. However, largely due to experimental and theoretical complexities, this technique has generally remained confined to academic institutions. Dr. Richter was recognized for his significant experimental advances and development of analysis procedures that will allow this technique to become more mainstream and suitable for industrial research applications.

Stephen Stranick will be awarded the **U.S. Department of Commerce Bronze Medal** in 2002 for his accomplishments in the areas of visible NSOM metrology. This non-destructive, nanometer-scale chemical characterization technique will undoubtedly be a key metrology that will continue to grow in importance and impact key applications in the fields of materials science, nanotechnology, molecular electronics, and high throughput experimentation. Dr. Stranick's scientific research and technical leadership has provided a conduit for the transfer of this enabling measurement technology to U.S. industry, positioning them to reap the many benefits from its implementation.

The team of **Stephan Stranick**, **Chris Michaels**, and **Lee Richter** will be presented with the NIST **Samuel Wesley Stratton Award** for 2002. The Stratton Award, first presented in 1962, recognizes an unusually significant research contribution to science or engineering that merits the acclaim of the scientific world and supports NIST's objectives. The Division 837 team received the award as a result of the impressive scientific advances that they have achieved in the areas of visible near-field scanning

optical microscopy (NSOM) metrology, Raman NSOM, and infrared (IR) NSOM. Their efforts have positioned NIST as a world leader in chemical-imaging NSOM, built strong alliances with the U.S. Chemical Industry, and lead a team to impact new technology frontiers of strategic interest to Chemical Science and Technology Laboratory (CSTL).

Cedric Powell was presented with the American Vacuum Society Albert Nerkin Award in 2001. The AVS Nerkin Award recognizes outstanding contributions to the solution of technological problems in areas of interest to the AVS. Dr. Powell was recognized “for the development of improved data, particularly electron inelastic mean free paths, for applications in quantitative Auger electron spectroscopy and X-ray photoelectron spectroscopy”.

Interactions:

The Division is involved in advisory and technical efforts with other government organizations including EPA, IAEA, NSF, TSA, and DoD. Close relations are maintained with national (e.g., ASTM, ANSI, MAS, EMSA, NFPA) and international (e.g., ISO, IUPAC, IAEA, VAMAS) organizations. The Division also maintains extensive interactions with private industry including: Charles Evans & Assoc., Dow Chemical, Dow Corning, DRI, DuPont, ExxonMobil, Honeywell, McCrone Assoc., Noran, Peabody Scientific, Pfizer, Photon Imaging, Schafer Vallecitos Laboratories, SRI, 3M, Visteon, and XOS, Inc; and academic partners including Cornell, George Mason, Lehigh, Penn State, Univ. of Rochester, University of California at San Diego, Univ. of Illinois, Univ. of Maryland, and Univ. of Texas at Austin, Univ. of Texas at Dallas.

Development of Accurate Quantitative Analysis Procedures for High-Angle X-Ray Emission Spectroscopy

CSTL Program: Technologies for Future Measurements and Standards

Authors: *J.T. Armstrong, and J.A. Small*

Abstract: A practical series of analytical and quality control procedures were developed and an evaluation of microprobe correction algorithms was made to provide a robust method to enable quantitative x-ray microanalysis to be performed at large, variable specimen tilt angles relative to the electron beam and x-ray detectors. The procedures and corrections explored were designed specifically to enable electron backscattered diffraction analysis (EBSD) and quantitative x-ray emission analysis (EDS/WDS) to be performed simultaneously on commercial scanning electron microscopes. They also enable integration of quantitative EDS/WDS with a variety of other surface and microanalysis techniques, such as Auger electron spectroscopy, x-ray photoelectron spectroscopy, and scanned probe microscopies. For the first time these procedures enable analysts to perform, simultaneously, accurate elemental analysis along with the best of the modern surface analysis methods. The beneficiaries of these procedures are microanalysts in a wide variety of commercial and homeland security applications from pharmaceuticals and microelectronics to explosives and forensic analyses.

Purpose: Electron backscatter diffraction (EBSD) is an important new analytical technique for micro- and nano-scale characterization of crystalline materials in scanning electron microscopes and similar instruments. There are several commercial manufacturers of EBSD detectors and this technique is being actively used for crystalline phase identification and phase orientation mapping of advanced materials with important commercial and defense applications. To properly characterize unknown materials, it is often critical to combine EBSD with quantitative x-ray emission (EDS/WDS) analysis; in most cases, the practical requirement is that these measurements be done simultaneously. However, EBSD analysis needs to be performed with the sample inclined so that the electron beam strikes it at a shallow angle (typically 20° above the surface plane); at such tilt angles, conventional correction procedures for x-ray analysis are not accurate and there are no generally agreed-upon alternatives. We have initiated a program, funded in FY 2002 as a CSTL exploratory research project, to determine the best analytical methodology, quality assurance testing, and data correction procedures to employ for high-tilt-angle EDS/WDS.

Major Accomplishments: We have performed extensive Monte Carlo calculations of electron trajectories in solid targets inclined at various angles with respect to the electron beam. We have tested these with experimental measurements made on our analytical scanning Auger microprobe, which is specially configured for doing x-ray emission analysis of inclined specimens. Preliminary measurements were also made on our field-emission scanning electron microscope with EBSD. These two instruments, because of the different azimuthal angles at which the x-ray detectors are mounted, represent the extreme conditions under which EBSD measurements are made. The experimental results are in good agreement with the Monte Carlo calculations, but show relatively poor

agreement to several empirical corrections that had been adapted for shallower beam tilt angles. The peak-to-background ratio for x-ray lines with large overvoltage ($U = E_0/E_c > \sim 3-4$) at high tilt were found to be within 10% of the values measured at normal incidence, suggesting that the correction method for particles and rough surfaces proposed by Small could be employed for tilted samples as well under these conditions. However, the measured peak-to-background ratio for higher energy lines ($U < \sim 3$), at high specimen tilts, differs significantly from the values measured at normal incidence. The Monte Carlo simulation results indicate that polynomial “a-factors” (such as developed by Armstrong for normal incidence thick specimens and microparticles) could be tabulated and employed in a simple-to-use correction procedure. Demonstration matrices were calculated and found to produce accurate results. In performing the experimental measurements, we found that great care was needed to properly reproduce the correct sample and detector positions. The x-ray path length (and thus the amount of x-ray absorption, vary significantly with detector azimuthal position, sample tilt (in both x and y directions) and sample z-positioning (height). The analytical results are highly sensitive to these factors.

An easy to use internal standard quality assurance check was developed to ensure reproducible positioning. A polished specimen of SRM 482 AuCu is mounted with the sample. Using the AuCu standard, the ratio of the Au-L to Au-M and Au-M to Cu-K are measured. These ratios are very sensitive to beam, specimen, and detector geometry. Reproducing these ratios to a set value assures a consistent geometry, which enables Monte Carlo based corrections to be used to process analytical data.

Impact: Development of analysis and correction procedures enabling quantitative EDS/WDS analysis at high specimen tilt angles answers several of the most critical current microanalysis needs of industry. It enables simultaneous quantitative x-ray emission and EBSD analysis and phase orientation mapping. The quality assurance approach allows microanalysts to consistently operate at defined analytical geometries. The results of this project also enable x-ray emission analysis to be performed simultaneously with other complementary techniques that typically have tilted samples such as Auger electron spectrometry, dual beam FIB, x-ray photoelectron spectroscopy, and the various ion, laser and scanned probe techniques. By not requiring the electron beam to be perpendicular to the sample surface, these techniques enable development of hybrid and miniaturized instruments that would be still capable of high-accuracy x-ray analysis. Application of this approach can aid industry in many areas including improved quality control, failure analysis, process control, device fabrication, polymer and biomaterials characterization, etc.

Future Plans: This work completed a one-year feasibility study conducted as an exploratory research project. The results are promising enough to warrant future work. We plan to distribute polynomial a-factor correction matrices to the microanalysis community from our best Monte Carlo calculations of x-ray depth distributions for systematic binary element compositions at specific high specimen tilt angles. We hope to continue to test and refine these corrections and our analysis and quality assurance procedures by standards testing with our field emission scanning Auger and scanning

electron microscopes. We plan to publish these methods once they have been refined and demonstrated to be robust.

Effects of Backscattered Electrons on the Lateral Resolution and Analysis Area of a Scanning Auger Microscope

CSTL Program: Technologies for Future Measurements and Standards

Authors: *C.J. Powell, S.A. Wight, and J.T. Armstrong*

Abstract: The lateral resolution, δr , is a critical parameter in a scanning Auger microscope (SAM) since it is a measure of the distinguishability of small objects. For quantitative interpretations of Auger-electron signals, however, it is also necessary to consider the analysis area (the area from which all or a defined percentage of the detected signal originates).

We have determined δr from linescans across a chemical edge for our newly acquired SAM at beam energies between 10 keV and 25 keV. These linescans also showed "tails" due to the effects of backscattered electrons. While these tails do not significantly affect the lateral resolution, they considerably increase the analysis area over simple expectations (e.g., that this area should be a small multiple of $\pi(\delta r)^2$). This increase of the analysis area will significantly influence Auger analyses of particles and inclusions.

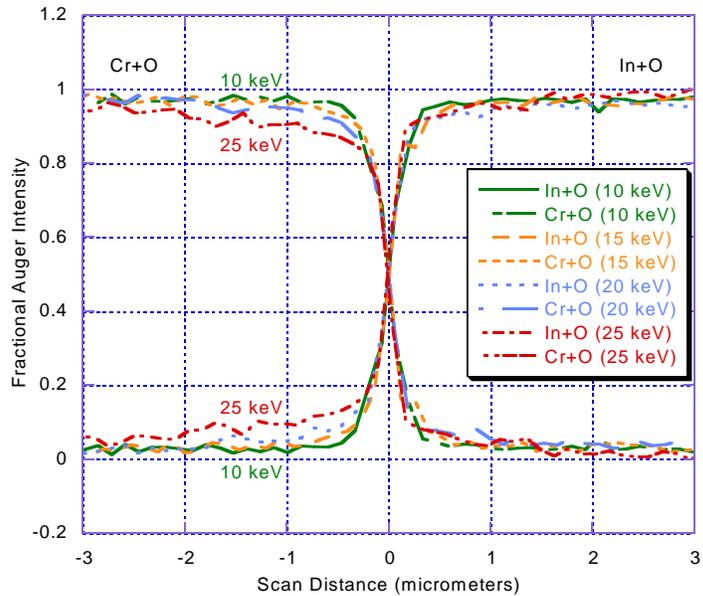
Purpose: To provide needed data and reliable models for more accurate surface, interface and particulate analyses by Auger-electron spectroscopy and X-ray photoelectron spectroscopy.

Major Accomplishments in FY2002: We made measurements of δr using a commercial magnification standard at beam energies of 10 keV, 15 keV, 20 keV, and 25 keV. The magnification standard consisted of lines of chromium and chromium oxide of varying widths and separations on an indium-tin-oxide coating that was deposited on a fused silica substrate. After light sputtering of the sample, Auger spectra were measured as the incident beam (at an angle of 55° with respect to the surface normal and parallel to a line) was scanned across an edge of the line. The Auger spectra measured between 300 eV and 600 eV consisted primarily of overlapping features due to chromium and oxygen on one side of the edge and to overlapping features due to indium and oxygen on the other side of the edge. We found that the Auger spectra in the vicinity of the edge could be satisfactorily fitted to linear combinations of In+O and Cr+O reference spectra measured far from the edge.

The Figure shows the fractional intensities of the In+O and Cr+O component Auger signals as the beam was scanned across an edge for each of the four beam energies. At each energy, there is a rapid change in the Auger intensities in the vicinity of the edge and slow changes ("tails") away from the edge. The rate of change of the Auger signals in the vicinity of the edge is related in part to the width of the beam and in part to the intrinsic sharpness of the chemical edge as well as to multiple scattering of the incident electrons, backscattered electrons, and Auger electrons in the vicinity of the edge. A Gaussian function could be fitted to the derivative of each linescan to give full-widths at half maximum (FWHM) intensity, measures of δr for these experiments, ranging from 540 nm at 10 keV to 456 nm at 25 keV. These FWHM values are appreciably larger than

the values of 13 nm at 10 keV and 7 nm at 25 keV, found in separate resolution tests with gold islands on a carbon substrate, that provide measures of the beam widths for the particular beam current used here.

Figure 1. Auger linescans showing the relative fractions of the In+O and Cr+O Auger signals as a function of scan distance across a line edge of a magnification standard for beam energies of 10 keV, 15 keV, 20 keV, and 25 keV.



The Auger signals away from the edge (the "tails" in the Figure) increase in intensity with increasing beam energy. Model calculations show that these tails are due to Auger electrons arising from inner-shell ionizations caused by backscattered electrons. As expected, the tails for a beam energy of 25 keV are more extended than those for lower energies because the average radii of sufficiently energetic backscattered electrons increase with beam energy.

The tails in Fig. 1 do not appreciably affect the determination of δr . Nevertheless, these tails greatly increase the analysis area. As the beam energy increases, the analysis area (e.g., the area from which 95% of the detected Auger signal originates) increases and can be appreciably greater than a small multiple of $\pi(\delta r)^2$, as indicated by model calculations. This increase in analysis area needs to be considered in quantitative Auger microscopy, particularly for "spot" analyses of particles or small inclusions.

In practical applications, the beam energy needs to be selected from a compromise among δr for the experiment (a convolution of the intrinsic beam width and the edge sharpness of a particular chemical phase in the specimen of interest), beam current, expected Auger signal intensity (sensitivity), and analysis area for the particular application (determined from the tails due to backscattered electrons in a linescan).

Impact: These experiments and associated model calculations give guidance on the analysis area relevant to Auger analyses of particles and small inclusions.

Future Plans: It is planned to perform Monte Carlo simulations for the conditions of the above experiments. Simulations of this type should give quantitative information on the analysis area for these and related experiments.

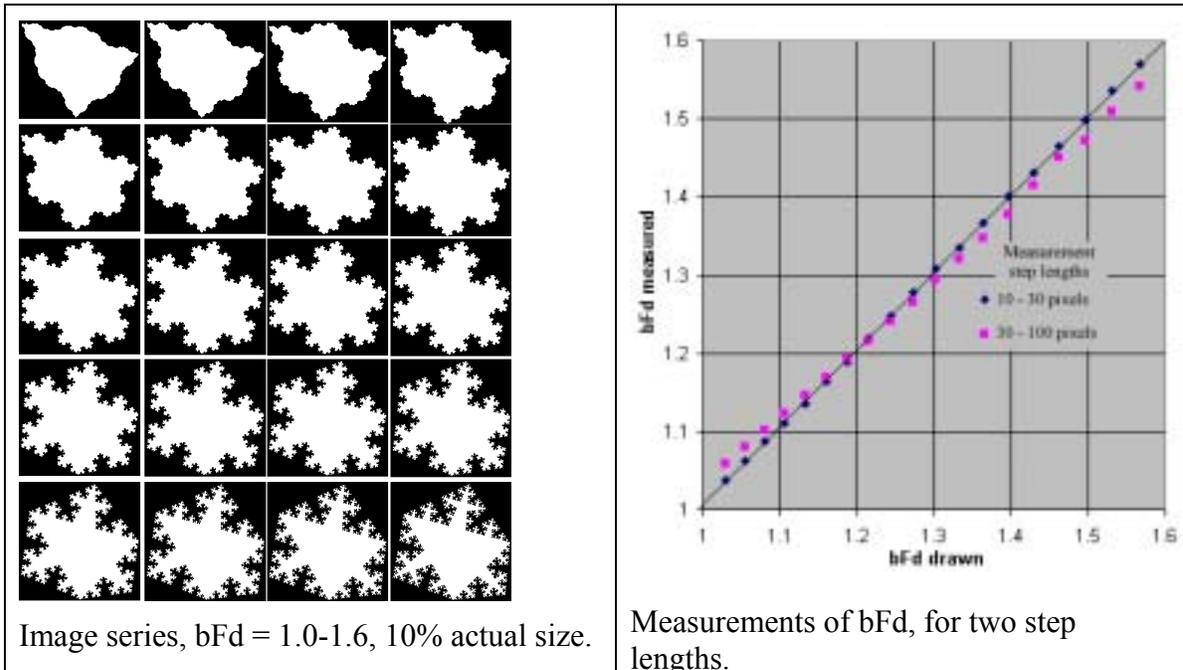
Images of Particle-Like Fractals with Differing Shapes and Boundary Fractal Dimensions for Testing Algorithms that Measure Fractal Dimension

CSTL Program: Technologies for Future Measurements and Standards

Author: *D.S. Bright*

Abstract: The shape of a single particle may indicate its treatment, chemical composition, or place of origin. Microscopists continually seek numerical parameters that quantify shape in order to characterize and classify particles. The boundary fractal dimension, **bFd**, is a parameter that describes the roughness of the outline of the silhouette of an object. Investigators have started to use the bFd in geology, tribology, pharmacology, medical research, aerosol science and food science. However, the values bFd from objects in digital images differ, depending on the measurement method, and hinder broader acceptance of the bFd. Investigators have tested their methods only on a few well known fractals, and these fractals sometimes even have dimensions outside the range of the dimensions measured for their samples. Sets of images were made available covering a wide range of bFd that were generated from a family of fractals related to the Von Koch snowflake. This family covers the full range of bFd, 1.0 – 2.0, and has a range of shapes for each bFd. Not all of the fractals give suitable particle-like fractal images. Suitable images, their bFd values, and the software used to make any fractals from the family and measure bFd from their images are available at:

<http://www.nist.gov/lispix/Lx04Doc/img-sets/Koch-fractal/koch-dnld.html>



Purpose: To provide images of fractals with a wide range of bFd and a variety of shapes. To characterize measurement methods using these images. It is hoped that the variety and complexity of these standard images can be used as a robust test for image analysis methods applied to real-world particles.

Major Accomplishments: Image sets of known bFd were generated and characterized. Only a few fractals or sets of fractals with very similar shapes have been available before. This standard set of images, as well as the measurements and software to generate and measure the images are available on the NIST web. This provides a set of standard reference images and algorithms for testing and developing fractal dimension analysis for imaging systems.

Impact: The images and bFd values will help investigators to characterize the accuracy of their fractal dimension measurement methods so that results can be compared and reliably used. This should promote use of and confidence in bFd measurements to characterize particles.

Future Plans: Include more image sets of fractals with a wider range of sizes and shapes, and with multiple fractal dimensions, that is where the bFd changes with step length. Unlike fractals, most real samples do not have just a single bFd for all length scales. Therefore, the bFd values must be associated with a step length that gives the scale of the measurement.

Preliminary Evaluation of Positive Secondary Ion Yield Enhancements Using Chlorodifluoromethane and Tetrachloroethene Backfilling

CSTL Program: Microelectronics

Authors: *P. Chi, and G. Gillen*

Abstract: Positive secondary ion yields in Secondary Ion Mass Spectrometry (SIMS) are strongly enhanced by the presence of reactive gas species. Oxygen primary ion bombardment or oxygen gas backfilling of the analytical chamber is commonly used for this purpose. However, for some metal elements such as Nb, Mo, Ag, and Cd, oxygen bombardment or gas backfilling does not enhance the ion yields. Recently, a experiments using SF_5^+ primary ions suggested that a fluorinated sample surface might provide some level of secondary ion signal enhancement. However, SF_5^+ primary ion beams are not generally available on commercial SIMS instruments. This has led us to explore alternative methods for enhancing ion yields by backfilling the sample surface with either chlorodifluoromethane (freon) or tetrachloroethene (C_2Cl_4) gas while depth profiling with an argon primary ion beam. These two reactive gases were found to significantly enhance secondary ion yields for many elements providing higher sensitivity for trace analysis by SIMS.

Purpose: Positive secondary ion yields in Secondary Ion Mass Spectrometry (SIMS) are strongly enhanced by the presence of reactive gas species. Oxygen primary ion bombardment or oxygen gas backfilling of the analytical chamber is commonly used for this purpose. However, for some metal elements such as Nb, Mo, Ag, and Cd, oxygen bombardment or gas backfilling does not enhance the ion yields. Recently, a experiments using SF_5^+ primary ions suggested that a fluorinated sample surface might provide some level of secondary ion signal enhancement. However, SF_5^+ primary ion beams are not generally available on commercial SIMS instruments. This has led us to explore alternative methods for enhancing ion yields by backfilling the sample surface with either chlorodifluoromethane (freon) or tetrachloroethene (C_2Cl_4) gas while depth profiling with an argon primary ion beam.

Major Accomplishments: Figure 1 shows a depth profile of 12 metal ion species at various freon backfill pressures. Most elemental secondary ion signals increased by one order of magnitude as the freon backfill pressure was increased from the 6.7×10^{-3} Pa to 2.7×10^{-4} Pa. Ion yield enhancements for 15 metal species under 2.7×10^{-4} Pa freon and tetrachloroethene backfilling are listed in Table 1. The yields for Al, Fe, and Cu are lower while Si and Ni are unchanged under freon backfill as compared with oxygen backfill. However, the yield for Mg, Ti, V, Cr, Mn, Zn, Nb, Mo, Ag, and Cd with freon backfill was several times higher than that of oxygen. The yield enhancement for Mg, V, Cr, Mn, Zn, Nb, Mo, Ag, and Cd were also higher with tetradichloroethene backfill, but the yields for Al, Si, Ti, Fe, Ni, and Cu were slightly lower as compared with freon backfilling. The sputtering rate under freon and tetradichloroethene flooding is about 2.5 and 1.6 times faster, respectively, than oxygen flooding under similar sputtering conditions.

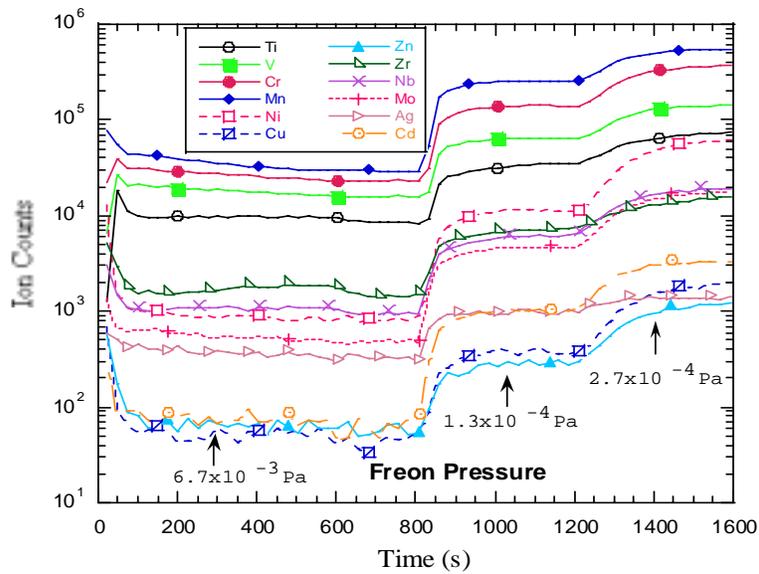


Figure 1: Depth profile for 12 metal ion species

Impacts: The results indicate that compared to oxygen backfilling, it is advantageous to use either freon or tetradichloro-ethene gas backfilling for enhancing the secondary ion yields in SIMS for many metallic elements. Except for Al, Fe, and Cu, the yields are several times higher for on most metal elements. The higher erosion rate using these gases also allows for more rapid depth profiling analysis.

Element	Ion Yields for Freon backfill norm. to O ₂ backfill	Ion Yields for Tetrachloro-ethene backfill norm. to O ₂ backfill
Mg	52	25.8
Al	0.7	0.62
Si	1	0.58
Ti	2.5	0.97
V	3.4	1.72
Cr	2.8	1.31
Fe	0.8	0.53
Mn	2.7	1.40
Ni	1.1	0.41
Cu	0.4	0.35
Zn	4.9	1.51
Nb	8.9	1.50
Mo	N/A	3.22
Ag	5.0	4.30
Cd	10	7.70

Table 1: Secondary ion yield enhancements of multi-elements under freon, tetrachloroethene (C₂Cl₄) that ratioed to oxygen backfilling

Future Plans: Taking advantage of a unique NIST triplasmatron ion source for producing fluorinated primary ion beams, these experiments will be extended to study ion yield enhancements of metal species using an SF₅⁺ primary ion beam.

Precision Isotopic Measurements with the NIST High Performance Secondary Ion Mass Spectrometry Facility

CSTL Program: Forensics and Homeland Security

Authors: A.J. Fahey

Abstract: The specific isotopic ratios of an element in a sample can, in some cases, be used to determine the history of a sample, its age, or its place of origin. In order for isotopic ratio data to be useful it often must be determined to a precision and accuracy of less than 1 part-per-thousand. To this end we have characterized the new NIST ims-1270 secondary ion mass spectrometer and its subsystems for high precision measurements of isotopic ratios.

Purpose: The purpose of this work is to measure isotopic ratios with high precision and accuracy in order to characterize microscopic quantities of materials.

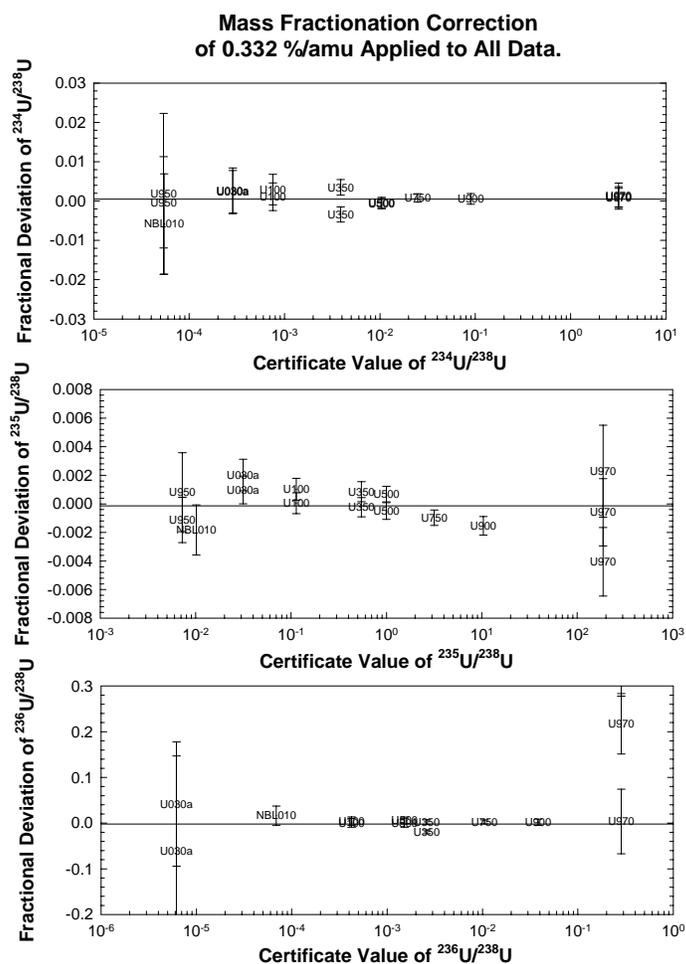


Figure 1. Deviation in $^{235}\text{U}/^{238}\text{U}$ isotope ratios from certified values.

Major Accomplishments:

Samples of known chemical and isotopic composition are available in the form of U_3O_8 as standard reference materials. These SRM's are unique in that they span more than 4 decades in their major isotope ratio. In order to characterize the ability of the ims-1270 at NIST to measure uranium isotopic compositions precisely and accurately, a selection of uranium SRM's were measured where the abundance ratio $^{235}\text{U}/^{238}\text{U}$ ranged from ~ 190 (highly enriched) to $\sim 0.7\%$ (natural). Combined with the minor isotopes of uranium, this scale of variation allows us to nearly span the dynamic range of the pulse-counting detection system. In addition, it allows us to test the reproducibility of the mass fractionation for isotopic ratio measurements on particles.

Figure 1 shows the deviations of each of the measured isotopic ratios for the available uranium

SRM materials as a function of the certificate values for each SRM. The data shown in Figure 1 was taken over a period of four months from May to September of 2002. A constant mass fractionation was applied to all of the data. Nearly all of the data points lie within one standard error of the mean for each of the isotopes and SRM's. There are two exceptions to this and the reasons for each are well understood. There is a trend in the $^{235}\text{U}/^{238}\text{U}$ values that is apparently dependant on the isotopic ratio. This is due to the fact that there is a non-linearity in the response of the electron multiplier detector used to count the ions. This effect has been documented by others including the group at New Brunswick labs that currently curates these SRM's. The magnitude of this non-linearity is very small, approximately 4 parts per thousand spanning more than 4 orders of magnitude (i.e. <1 ppm). The other significant deviation from the certified value lies in the measurement of ^{236}U for the SRM U970. This isotope of uranium, ^{236}U , is the least abundant isotope in all of the uranium SRM's, and in U970 it is the most difficult to measure because of an unresolvable interference due to ^{235}UH . Although the hydride interference correction can be made reliably for most of the SRM's the U970 is unusual because of its very high abundance of ^{235}U , generating a large ^{235}UH signal, and its low abundance of ^{238}U (the ^{238}UH signal is used to correct for the interference of ^{235}UH at the mass of ^{236}U). However, by using the "cold trap" on the ims-1270 sample chamber we can reduce the hydride interference enough to make an accurate correction. This is evident in Figure 1 where the two points for U970 in the ^{236}U plot were measured one with the "cold trap", and one without.

Impact: The measurements reported here show that the new NIST ims-1270 is capable of high precision and accuracy measurement of U_3O_8 particles. The mass fractionation is stable and reproducible and corrections can be made reliably for hydride interferences. This will aid in our support of the IAEA for monitoring signatories of the Nuclear Non-Proliferation Treaty.

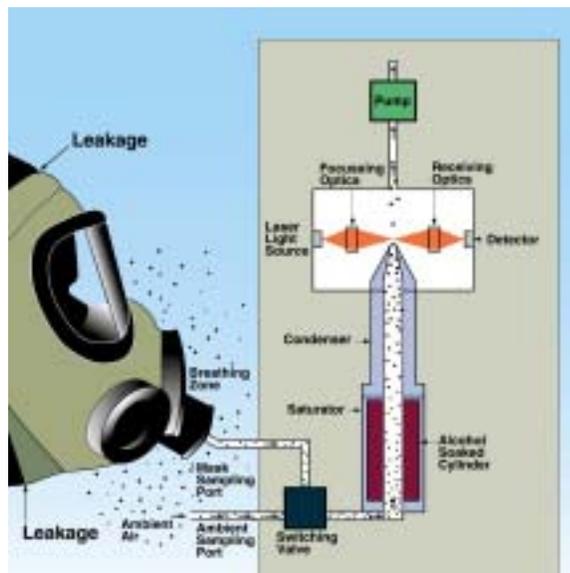
Future Plans: Plans are in place to explore measurements of other isotopic systems. Isotopic ratios of oxygen, carbon, sulfur and other elements will be used to identify the origins and histories of materials and commercial products.

Verification of Calibration Procedure for Testing Military Gas Masks

CSTL Program: Forensics and Homeland Security

Authors: *R. Fletcher, L. King, and J. Small (837); M. Winchester (839); and J. Yang, and G. Mulholland (866)*

Abstract: Military personnel wear gas masks for protection against a chemical and biological assault. The recognized potential global threat from chemical and biological agents demands that effective defense measures be taken. An important part of this defense strategy is the testing and verification that assures secure gas mask fits. The M41 was developed for the military to field-test its protective equipment on the person using the protective devices. The Army determines the gas mask fit quality by measurement and comparison of the ambient aerosol concentration outside of the fitted masks to the aerosol concentration inside. The particles can identify both leaks in the mask and inefficiencies in the filters. The fit test procedure is illustrated in the Figure. This technology is believed to provide a complete diagnostic of the integrity of the mask, the filter and the fit on the individual.



With present technology and the transient nature of aerosol, a certified reference material for aerosol concentration has not been feasible. NIST is to verify the accuracy of the calibrant by comparison measurements by a primary particle counting approach using electron microscopy and a secondary approach of determining the particle concentration in terms of electrical current using an aerosol electrometer.

Purpose: The objective is to provide measurement assurance to the U.S. Army for their gas mask fit-test method by verifying the accuracy of the aerosol concentration measurement integral to this test method. The Army, working with TSI, Inc., an aerosol instrument manufacturer, has developed the M41 Protective Assessment Test Systems (PATs) to test and verify the goodness of fit for the gas mask on the individual person that is issued the device. The M41s are tested and verified by the U.S. Army Test,

Measurement, and Diagnostic Group using a fit-test calibration stand (test stand). The components of the test stand are an aerosol generator, aerosol electrical charger, a mobility classifier to produce monodisperse 80 nm diameter aerosol, an aerosol dilution system and two condensation particle counters (CPCs). The test aerosol concentration range is 100-10,000 particles/cm.³ The CPCs serve as the calibrants in the test stand for the M41s. There are no aerosol concentration standards for the CPCs nor are there certified reference materials available for aerosol concentration standardization. The measurement process currently has no links or traceability to a standards granting organization. The U.S. Army Test, Measurement, and Diagnostic Equipment Activity (USATA) requires the development of an aerosol concentration standard method, traceable to the National Institute of Standards and Technology.

Major Accomplishments: We have completed the work that provides a NIST traceable calibration for the aerosol electrometer. This allows us to verify the voltage response for known femtoampere current inputs. We have finished the calculations to simulate particle loss in the CPC. Electron microscopy has been completed on quantitatively collected 80 nm particles over a concentration range of approximately 200 particles/ cm³ to 10,000 particles/cm³.

Impact: This verification and possible development of a standard method would enable the accurate calibration of Condensation Particle Counters that are currently used to calibrate M41 Protective Assessment Test Systems (PATS) for the Army. The Army serves as the sole calibration agent for the tri-services. This project is also directly relevant to homeland security as the procedures developed here are applicable for verification of instruments used to fit test gas masks and protective suits used by first responders and emergency response personnel.

Future Plans: The project is a two-year effort and is essentially completed. Some additional stability testing and measurement issues associated with uncertainty determination are planned.

Characterization of Trace Explosive Detection Equipment for Airport Security Applications

CSTL Program: Forensics and Homeland Security

Authors: *G. Gillen, R. Fletcher, S. Wight, S. Roberson, E. Etz, A. Lindstrom, C. Zeissler, and J. Verkouteren (837); B. Benner (839); and R. Lareau (Transportation Security Agency)*

Abstract: In collaboration with the Transportation Security Agency's (TSA) Trace Explosive Detection Group, the Chemical Science and Technology Laboratory (CSTL) has been working to build a chemical metrology program to help support the widespread operational deployment and effective utilization of trace explosives detection devices throughout the United States. A second objective is to develop, at NIST, the specialized measurement expertise that will be needed to support the development of the next generation of explosive detection equipment. The low volatility of most high explosives makes direct analysis of vapors impractical. Therefore, most detection systems are based on either airborne or surface swipe collection of micrometer-sized explosive particles with subsequent thermal vaporization of the particles into an ion mobility spectrometer for identification. The effective collection and thermal desorption of the explosive particles is the critical front-end process for the successful and reproducible detection of explosives. CSTL is utilizing existing expertise in particle analysis, analytical chemistry and chemical microscopy to study this process in detail.

Purpose: Current aviation security legislation requires the unprecedented utilization of trace explosives detection systems for screening of baggage, cargo and passengers at US airports in support of Homeland Security. CSTL is responding to the growing metrology requirements for trace explosive screening by leveraging existing NIST expertise in particle analysis, analytical chemistry and chemical microscopy to build a measurement infrastructure for the continued development, characterization, calibration and standardization of trace explosive detection devices. The majority of explosive detection systems rely on the collection of micrometer-sized explosive particles collected on swipe samples (tabletop units commonly used at airport security checkpoints) or from airborne particle collection (next generation walk-thru portal detection systems). The low volatility of most high explosives makes direct analysis of vapors impractical. Collected explosive particles are thermally desorbed from the collection medium (cloth or steel mesh) into an ion mobility spectrometer (IMS) for identification. The effective collection and subsequent thermal desorption of explosive particles into the IMS is the critical front-end process for the successful and reproducible detection of explosives. In FY02, we initiated a new 3-year research program (through NIST's Advanced Technology Program Funding) to study this process in detail. A complete understanding of the operational parameters and limitations of trace explosive instruments is required for their effective and reliable operation.

Major Accomplishments: A number of experiments were initiated in FY 2002 to evaluate both swipe and portal-based explosive detection systems. A priority has been to study the factors involved in the release and effective collection of explosive particles in

portal systems. One current study involves the use of fluorescence optical microscopy to study the release of monodisperse, fluorescently tagged microsphere particles from model surfaces under an impinging air jet (as used in airborne collection systems). Preliminary data suggests that almost no particles with diameters less than ~ 6 micrometers are liberated under these sampling conditions. This information constrains the size of particles likely to be sampled using airborne collection techniques and will aid in the design of next generation explosive detection systems. The particle size collection efficiency of the metal collection filters used in portal systems is also being evaluated in this work. Another issue addressed this year was determining how to visualize a few individual explosive particles surrounded by millions of ambient aerosols on mesh filter collectors. For this purpose, new approaches for chemically specific imaging of explosive molecules were developed using the NIST cluster secondary ion mass spectrometry technique.

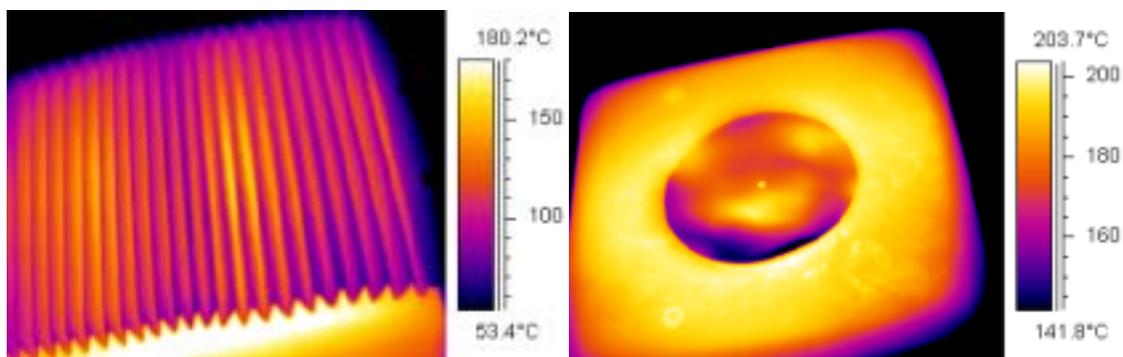


Figure 1(A). Infrared camera image of stainless steel mesh used in portal explosive detection unit.

Figure 1(B). Infrared camera image of swipe collection cloth.

A second major thrust has been to study the temperature dependence of explosive particle vaporization. In these experiments, secondary ion mass spectrometry, Raman microscopy and scanning electron microscopy have been used to study the temporal variations in chemical composition and morphology that occur during heating of individual explosive particles. Figures 1a and b demonstrate one component of this work. The figures show infrared camera images of two types of collection media used in commercial explosive detectors. The CSTL infrared imaging capability is used to provide precise non-contact and spatially-resolved temperature measurements of these surfaces. This information provides a unique method for relating the chemical degradation information obtained using our microanalytical techniques to the actual temperatures achieved during the sampling process.

Impact: Characterization of the performance characteristics of explosive detection systems is of significant importance for the transportation security agency and law enforcement. Optimized performance will help to ensure the safety of our transportation system, minimize possible security threats and provide a more robust tool for state and local law enforcement applications.

Future Plans: In the next fiscal year, the scope of the work begun this year will be expanded to include a variety of additional studies. A robust examination of particle generation and collection will be conducted as well as a detailed evaluation of the thermal degradation of various explosives. New analytical capabilities in ion mobility spectrometry, gas chromatography, mass spectrometry and optical and infrared microscopy are being added to support this effort.

Results of SiO₂/Si Comparison between Neutron Scattering and GIXPS

CSTL Program: Microelectronics

Authors: *T. Jach, and E. Landree*

Abstract: The metrology of gate dielectric films, an important consideration in CMOS semiconductor fabrication, crosses a new measurement threshold when film thicknesses are less than 10 nm. Recent comparisons using established techniques, or even different instruments of the same type, indicate that there are uncertainties in the measurements of simple SiO₂/Si films arising on this scale which far exceed the supposed precision of the individual methods. In addition to the inherent need to reconcile disparate measurements of SiO₂ films, the possibility for greater digressions arises as multilayer gate dielectrics are grown. Discrepancies between the results reported by different techniques begin to creep into measurements at the level of 10 nm for three different reasons. Some may occur because different physical properties are actually measured and the “thickness” defined by these methods starts to differ as the scale decreases. Secondly, the assumed values of physical parameters determining a measurement may be inaccurate on a scale that was not previously of concern. Finally, some techniques employ processes that may change the sample on the scale of interest. We are able to test the first two possibilities with a comparison measurement between grazing incidence x-ray photoemission spectroscopy and neutron reflectivity.

Purpose: The microelectronics industry is constrained to reduce the thickness of gate oxide layers as part of the overall scaling down of the dimensions of CMOS devices. The current thickness of these layers (and new materials being investigated to replace them) is of the order of 3 nm. There is currently no SRM on this thickness scale and methods that would be used to measure the thicknesses are not in agreement. We are investigating the metrology of very thin layers of SiO₂ by comparing two methods that are sensitive to the atomic characteristics of the layers. Other factors that we wish to observe are the effects of roughness and interfaces of the layers.

Major Accomplishments: During the past year we were able to complete measurements on a set of samples of SiO₂/Si in the thickness range of 3-7 nm. The methods employed, grazing incidence x-ray photoelectron spectroscopy and neutron reflectometry, are comparable techniques which rely on grazing angle beams scattering from thin surface layers. They differ, however, in relying on totally different physical interactions which depend, in turn, on different physical properties of the layer materials. Both methods provide values for the thicknesses of the layers, while being able to distinguish between the oxide layers and layers of contamination that may reside on the surface. We observe consistent differences between measurements made by the two methods. This is attributed partly to the difference in physical properties measured, and partly to the uncertainties about the correct physical values to use in determining thickness.

Impact: The results have been reported at several meetings targeting the metrology community for the semiconductor industry such as specialty meetings of the American Vacuum Society, the International Conference on Practical Surface Analysis, and

International SEMATECH. They have also been written up for publication and discussed with analytical lab managers for semiconductor companies. There has been recognition that the definition of gate thickness is dependent at this level on the method that is used to characterize it. Based on cited NIST results, Grazing Incidence X-Ray Photoemission Spectroscopy has been adopted as the method of choice for characterizing surface contamination on the Japanese research fabrication line dedicated to developing next generation process technology (400 mm Si wafers).

Future Plans: The characterization of SiO₂ layers has been ongoing for several years and has been completed. The results point to a need for more accurate values of optical constants, photoelectron effective attenuation lengths, and photoemission cross-sections for materials of interest in the semiconductor industry. These parameters are appropriate areas for improved measurement by NIST. The interest in replacing SiO₂ in gate dielectrics with high-k dielectric materials offers the possibility of rescaling the gate oxide to more manageable thicknesses, which would extend the current shrinking of device size for another ten years. The chemistry of high-k oxides (such as HfO₂) is very poorly known. Grazing incidence XPS and neutron reflectometry can be applied to study the density and interface characteristics of these materials.

Mass Determination From Particle Size and Number

CSTL Program: Environmental Technologies and Services

Authors: *J.R. Verkouteren (837); and A.G. Wylie (U. of MD)*

Abstract: The total particle mass of a population of asbestos fibers was determined from 2-dimensional measurements of length and width. A portion of a population deposited on a filter was measured from images collected on the SEM. The mass of each measured particle was calculated by assuming values for density and thickness. The fibers were classed into bins by length, width, and mass and the total numbers of fibers on the filter were calculated. All three frequency distributions were compared to a power-series to test the fractal model proposed for fragmentation in general, and asbestos in particular. The total mass was calculated both by summing the particles in each mass bin, and by integration of the fitted distribution. The calculated masses agree with the weighed mass, and provide support for the approach. This work provides a critical link between particle number and mass and provides the basis for a new method for determining low concentrations of asbestos in bulk materials. These issues are critical to the current review of asbestos regulations being conducted by the regulatory agencies, which are likely to result in new rule-making for asbestos.

Purpose: Regulatory agencies are currently reviewing their asbestos regulations to determine whether revisions are needed. The different agencies regulate on the basis of either mass or particle size/number, and a more cohesive approach is desired. In addition, a much lower threshold limit for mass is being considered that is below the detection limit of the standard method. Particle size, number, and mass are all related measures of a particle population, and the total mass can be determined if the distribution can be modeled. The particle size distribution of asbestos has been reported to follow a fractal distribution, and since the density is a constant, the mass must follow a fractal distribution. This study was designed to test the accuracy of the mass determination of an asbestos particle population from measures of particle size and number. If successful, this work would provide a needed link between mass and particle number, and would provide the basis for a new method for measuring low concentrations of asbestos in a bulk sample.

Major Accomplishments: A known mass of asbestos was deposited on a filter, and 50 randomly selected fields were imaged on the field-emission-gun SEM at three different magnifications. The fiber lengths and widths were measured, and the thickness calculated by assuming one-half the measured width. The fibers were binned by length, width, and mass and the total number in each bin over the entire filter was calculated. Overlap in the frequency of bins common to two magnifications indicated internal consistency in the calculation of total number. The frequency distributions were modeled by a power series, consistent with the fractal model proposed for asbestos. The total mass was calculated both by summing the particles in each mass bin, and by integration of the fitted distribution. Although there are very few particles in the large mass bin that contributes greatly to the total mass, their number is predicted correctly by the modeled distribution. Although we have not yet determined the uncertainty of the final mass

calculation, the values arrived at by the two different calculation are quite close to the weighed value, lending support to the overall approach.

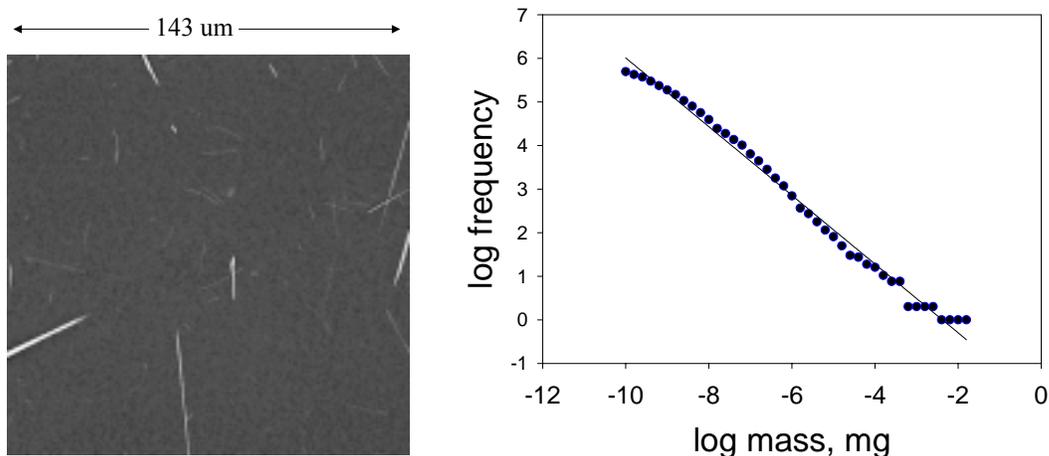


Figure 1. SEM fiber image and mass distribution of an asbestos fiber population

Impact: The immediate use of this work would be to develop a new quantitative method for bulk asbestos analysis based on measurements of particle size and number. This approach should lend itself to accurate measures of mass concentrations at 0.1%, which is the new threshold limit being discussed. Absent such a method, many new materials might be labeled as asbestos-containing based on the discovery of a few fibers and the inability to convert this correctly to mass concentrations. The long term impact of this work is to provide a new framework for asbestos regulations that relates the hazardous material (defined in terms of mass) with the risk (defined in terms of particle size/number).

Future Plans: This approach may be useful for assisting other laboratories in the development of a new method for bulk asbestos analysis. We plan to explore the possible applicability of this method for studying the distribution of asbestos aerosols in support of the NIST strategic focus on human health. A NIST exploratory research proposal has been written on this topic.

XML for Microanalysis

CSTL Program: Industrial and Analytical Instruments and Services

Author: *J.H.J. Scott*

Abstract: The purpose of this project is to enable the free exchange of spectral information among microanalytical instrument users by developing an XML-compliant markup language for spectroscopy data and to provide an information framework for storing and sharing microanalysis data community-wide, allowing more sophisticated theoretical model building and model assessment to take place. XML development efforts on this project focused carefully on the original scope of the project (creating a spectrum file format), but the eventual XML application was designed to integrate with future components such as sample information file formats and instrument information file formats without sacrificing its performance as a spectral exchange tool. After testing several variations of the markup language and exploring design tradeoffs, a working prototype was implemented to store test data. A summary of conclusions and recommendations from this study was presented at the Microscopy and Microanalysis 2002 Meeting. The presentation spawned a lively discussion and prompted several industry representatives to request involvement in future work and to suggest a task group be formed to coordinate a more coherent development effort. The formation of this group has begun and its output will be considered for submission to an appropriate standards body such as ASTM or ISO.

Purpose: Although the original goal of this work was to provide a standard file format for the exchange of spectral data between microanalysis laboratories, it quickly became clear that this technology could provide a framework for broader information sharing in the microanalysis community. A well-designed Microanalysis Markup Language (MML) can capture information about all aspects of a microanalysis experiment (not just spectral results). This has led to a natural convergence of this project and the SpectroML project led by Gary Kramer. Although the two formats remain distinct because of the specific information being represented, the inherent flexibility of XML ensures compatibility and interoperability between the two applications. Because XML-formatted data exchange in the x-ray spectrometry industry is still in its infancy, an important opportunity has arisen to work on an open standard format with all the manufacturers before a proprietary approach has taken hold. One express purpose of this work is to encourage consensus among the end users and x-ray analysis system vendors. Buy-in from both the analytical instrument users and the system vendors is critical to the success of this project.

Major Accomplishments: After testing several variations of the markup language and exploring design tradeoffs, a working prototype of the Microanalysis Markup Language (MML) was implemented to store test data. Variations using XML attributes in place of some elements were considered, but these were abandoned in favor of a more normalized approach. Details of the format were presented in the Frontiers of X-ray Spectrometry session at the Microscopy and Microanalysis 2002 Meeting this summer in Quebec City. The presentation spawned a lively discussion and prompted several industry representatives to request involvement in future work and to suggest a task group be

formed to coordinate a more coherent development effort. Following an impromptu group discussion after the talk and one-on-one meetings with vendors in the exhibit hall, it was agreed that a draft would be circulated for comment and revision.

Impact: In addition to sparking immediate interest among end users and industry representatives at M&M 2002, this work led to the reactivation of the Microbeam Analysis Society's computer activities subcommittee headed by Nestor Zaluzec at Argonne National Laboratory. This same committee helped develop the EMMFF file format, a simpler ASCII-based spectrum exchange format currently in use. XEDS manufacturers offered non-financial support and collaboration opportunities along with implementation suggestions and requests for features.

Future Plans: Future work on the markup language will attempt to refine and improve the implementation, taking account of the suggestions from the user/vendor task group after circulation of a draft standard. A small group of beta test sites and working microanalysis laboratories will be used to ensure the XML application is practical and not burdensome. If sufficient industry interest is shown, NIST will aid industry in developing a national and/or international standard through ASTM E42 or ISO/TC202.

```
<?xml version="1.0"?>
<experiment>
  <spectrum>
    <title>S8 Cu 20kV 20nA UTW</title>
    <date>2002-08-07</date>
    <time>11:45:00.0</time>
    <owner>John Henry Scott</owner>
    <xunits>keV</xunits>
    <yunits>counts/s</yunits>
    |
    <x-mm>0.0000</x-mm>
    <y-mm>0.0000</y-mm>
    <z-mm>0.0000</z-mm>
    <edsdetector>SIUTW</edsdetector>
    <spectrum-data>
      <frame npoints="2048">
        0.000    0.0
        0.010    3.0
        0.020    1.0
        0.030    6.0
        0.040    5.0
        0.050    8.0
        0.060    20.0
```

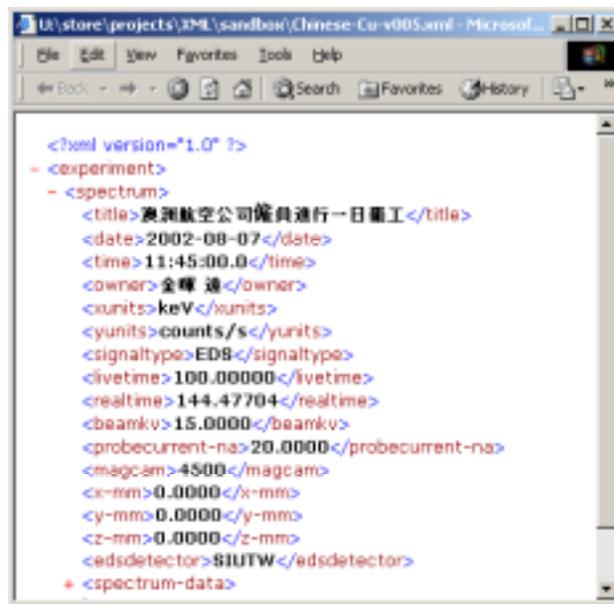


Figure 1. Example Microanalysis Markup Language (MML) excerpts showing element structure (left) and default browsing display in Internet Explorer (right).

Development of SiGe Compositional Standards for the Semiconductor Industry

CSTL Program: Microelectronics

Authors: *R.B. Marinenko, J.T. Armstrong, S.Turner, E.B. Steel, and D.S. Simons*

Abstract: Bulk SiGe wafers cut from single-crystal boules were evaluated with the electron probe microanalyzer (EPMA) for micro- and macroheterogeneity for use as primary standards for future characterization of SiGe thin films on Si that are needed by the microelectronics industry as reference standards. Specimens with nominal compositions of 14 and 6.5 atomic % Ge were rigorously tested with wavelength dispersive spectrometers (WDS) using multiple point, multiple sample, and duplicate data acquisitions. These data were compared to pure Si and Ge wafers tested under the same experimental procedures. The SiGe14 had the least heterogeneity with an overall expanded uncertainty (99%) of 1.6 % mass fraction or less for both elements while the SiGe6.5 specimen had an expanded uncertainty as large as 4.7 % mass fraction for Ge and less than 1.8 % mass fraction for Si. Next generation computer chips and most current cellular telephones are based on SiGe technology. Industry has requested a compositional standard to meet this growing industry usage. Industry data shows that their current accuracy of ± 10 atom percent does not meet required tolerances for their devices.

Purpose: SiGe technology is having a profound impact on the wireless and computer industries enabling the development of electronic components that are smaller, faster, less noisy, require less power, and are nearly as inexpensive to produce as silicon components with little retooling. With this new technology has come the need to characterize the thin films used in the new devices. We are working with the semiconductor industry to use the electron probe microanalyzer (EPMA), Auger analysis, analytical electron microscopy (AEM), and secondary ion mass spectrometry (SIMS) to develop bulk and thin film materials that can be used as compositional standards for SiGe thin film manufacturing.

Major Accomplishments: EPMA-WDS was used to test the heterogeneity of bulk SiGe wafers for use as primary standards in subsequent characterization of SiGe thin films on Si. SiGe wafers (ranging in sizes from about 200 to 900 mm²) cut from two different commercially available SiGe single-crystal boules (nominal compositions of 14 and 6.5 atomic % Ge in Si) were evaluated for the extent of micro- and macroheterogeneity.

After initial point beam line profiles of 2 mm steps, and random point analyses showed little heterogeneity, samples were cut up into smaller specimens of about 1 cm². Five specimens were each sampled at 7 randomly-selected points analyzed in

Heterogeneity Test for Si, Ge, and SiGe Wafers				
Expanded Uncertainty (99%) in % mass fraction				
Sample	SiK1	SiK5	GeL1	GeL5
StdWafers		0.94%	1.36%	0.60%
SiGe14	1.22%	1.29%	1.38%	1.55%
SiGe6.5	1.75%	1.55%	4.67%	4.64%

duplicate. Results were used to evaluate the within-specimen, between-specimen, and experimental uncertainties for each element and these in turn were used to calculate an overall uncertainty due to specimen heterogeneity. In the table are the expanded uncertainties for the two SiGe wafers compared to results (in the first row) obtained with the same testing procedure for pure Si and Ge wafers. Si and Ge were each analyzed on two different spectrometers. The SiGe14 wafer is the better standard for both Si and Ge, where the measured heterogeneity is about twice that of the pure wafers. The SiGe6.5 specimen may be usable if the larger uncertainty in the Ge heterogeneity is tolerable.

Impact: This work can provide the semiconductor industry with a needed SiGe bulk reference material that is the first step in providing the thin film reference material it needs for the manufacture of SiGe wireless and next generation microprocessor components.

Future Plans: Bulk chemistry of these SiGe specimens will be determined with Optical Emission Mass Spectrometry. The resulting bulk compositional data will then be used for the quantitative evaluation of the SiGe thin films on Si that the semiconductor industry needs as reference materials.

High Speed Elemental Mapping with the Silicon Drift X-ray Detector (SDD) on an SEM

CSTL Program: Technologies for Future Measurements and Standards

Authors: *D. Newbury, J. Small, and D. Bright*

Abstract: The silicon drift detector (SDD) is a new type of semiconductor energy dispersive x-ray spectrometer (EDS) capable of operating at much higher count rates than the conventional monolithic Si-EDS (at least 250 kHz instead of 25 kHz). This speed enables practical realization of “spectrum imaging” for x-ray mapping, in which the entire x-ray spectrum is recorded at each picture element of the map with a dwell time as short as 10 ms. The resulting data array can be interrogated at any time after collection to measure any constituent of interest. The availability of the complete spectrum enables quantitative mapping, including background and peak overlap correction critical to robust, meaningful minor and trace constituent mapping.

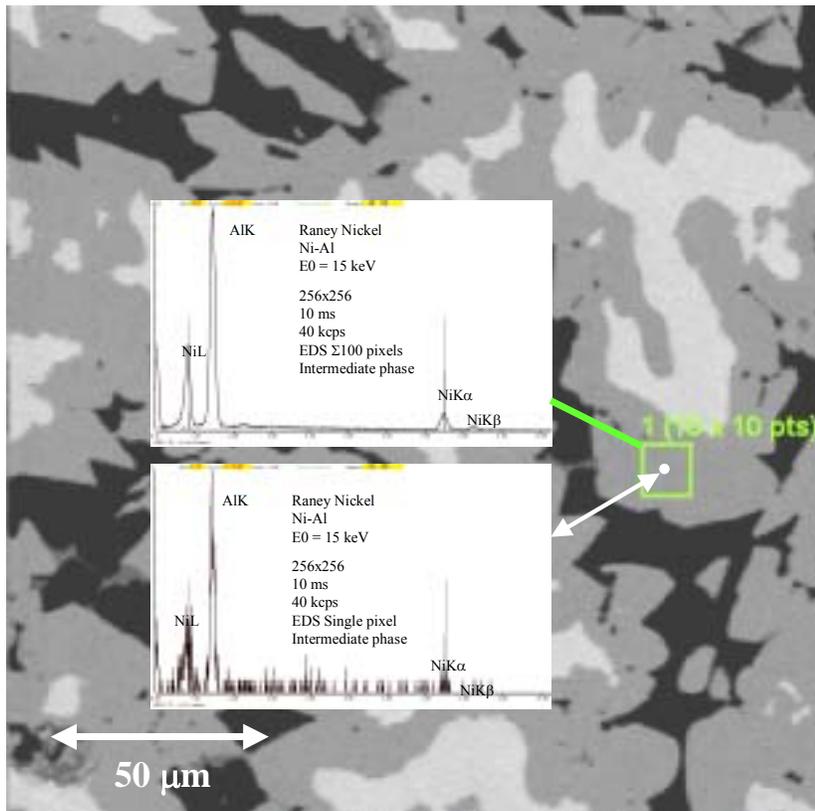
Purpose: Chemically-differentiated microstructures arise because most mixtures of two or more elemental species tend to separate into two or more compositionally-distinct phases at the micrometer to nanometer spatial scale. Compositional mapping by electron-excited x-ray spectrometry with the scanning electron microscope/energy dispersive spectrometer (SEM/EDS) is one of the most widely used techniques for the study of microscopically heterogeneous materials. Existing x-ray mapping techniques are severely constrained by the count rate limitations of conventional Si-EDS.

Major Accomplishments: A high count rate SDD developed through Phase I and II NIST/DoC Small Business Innovative Research (SBIR) grants has been adapted to explore new aspects of x-ray mapping. Spectrum imaging (SI), a powerful advance on conventional x-ray mapping, has been successfully demonstrated with the high speed data stream of the SDD. In the SI mode, the beam is addressed to dwell for a specified time at a picture element (pixel) and a complete 2048 channel EDS spectrum is recorded, thus creating a database array [$m \times n \times I(E)$] of m rows by n columns by intensity vs. photon energy [$I(E)$, 2048 channels]. The intensity per channel $I(E)$ of this spectrum can be recorded to a depth of 16 bits. Because of the increased SDD photon counting speed, rapid mapping can proceed with a pixel dwell time as short as 10 ms, giving a total mapping time of approximately 650 s for a 256x256 map. The SI mode permits the analyst to efficiently collect all the available spectral data with no loss and to subsequently interrogate the resulting data cube concerning any possible constituent of interest, even if questions arise long after the specimen has been removed from the SEM. Rigorous quantitative mapping procedures can be applied that make accurate background and peak deconvolution corrections to provide robust measures of minor and trace constituents, which are often misleading with conventional mapping procedures that rely only on “spectrum windows.” The figure shows an example of a compositional map of the microstructure Raney nickel, a methanation catalyst, with the recorded database spectra obtained from a single pixel (pixel dwell time 10 ms) and from a 10x10 square of pixels. Major constituents are readily visible in the single pixel spectrum, while the 10x10 square of pixels has sufficient counting statistics for minor and trace constituents.

As we develop the capability of operating in the SI mode at higher counting rates, even shorter pixel dwell times will become feasible.

Impact: Characterizing the chemical microstructure and relating this structure to macroscopic material properties (strength, toughness, hardness, etc.) and failure mechanisms (corrosion, fatigue, etc.) are central themes of modern materials chemistry/materials science. Real time x-ray mapping will significantly improve this critical characterization technique with broad applications in materials science.

Future Plans: The long range goal of the SDD project is to fully exploit the maximum counting capability of the x-ray detector, which appears to be in excess of 1 MHz. Currently the maximum useful data stream rate is being limited by the spectrum histogram binning process, either in the digital signal processor or in the computer software system for recording the SI database. On-going research through SBIR contracts is seeking to identify and overcome the spectrum processing limitations.



Compositional map of Raney nickel alloy, with spectra recorded at a single pixel (lower inset) and integrated over a 10x10 array of contiguous pixels (upper inset).

NIST Microcalorimeter Detector for High Resolution X-ray Detection

CSTL Program: Industrial and Analytical Instruments and Services

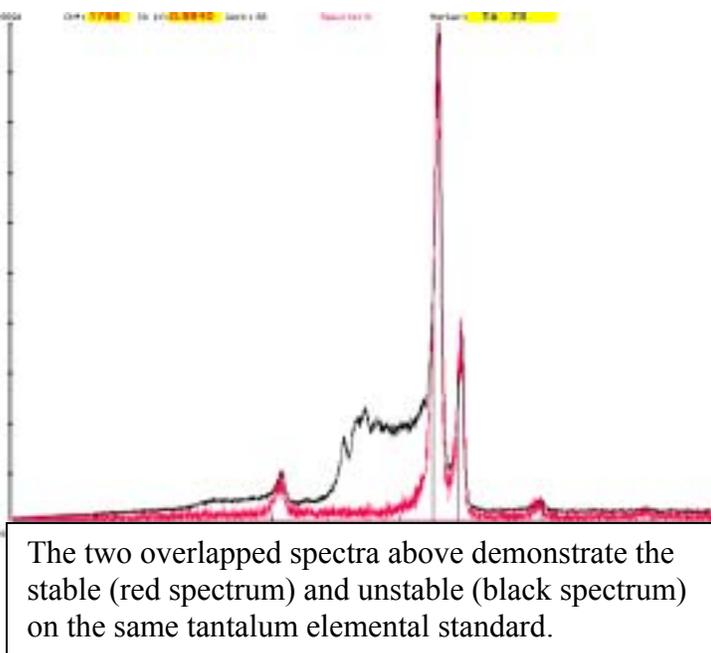
Authors: J.A. Small, D.E. Newbury, L. King, T. Jach, S.W. Nam, K. Irwin, and S. Deiker

Abstract: A NIST microcalorimeter energy dispersive x-ray spectrometer (μ cal EDS) has been successfully transferred from NIST Boulder to an analytical microscopy environment at NIST Gaithersburg. Routine operation and maintenance of the cryogenic and cryoelectronic systems has been taken over by Division 837 staff. Resolution performance of 9 eV or better has been achieved for short (~ 100 s) accumulations. Long term (>1000 s) measurements have been found to be subject to instability that limits accurate measurement of minor x-ray peaks. Division 837 researchers are currently working with NIST Boulder to diagnose the problem(s) and design corrective measures to improve the detector stability during long analysis times.

Purpose: (1) Transfer the μ cal EDS from the development laboratory (Boulder) to an analytical laboratory (Gaithersburg); (2) Evaluate the day-to-day cryogenic and cryoelectronic operation of the detector in a “user” environment; (3) Use the new detector to support critical chemical measurement efforts for microanalysis research.

Major Accomplishments: A NIST μ cal-EDS has been successfully installed on an analytical SEM in Div. 837. Staff learned the cryogenic and cryoelectronic operation and maintenance of the detector. However, the detector remains, on the whole, an experimental instrument. There are several limitations that we have observed and are in the process of correcting. Initial measurements demonstrated resolution of 9 eV or better (at $MnK\alpha$ and 40% deadtime) for short duration accumulations (100 s), suitable for measurements of major (concentration, $C > 0.1$ mass fraction) and minor ($0.01 \leq C \leq 0.1$ mass fraction) constituents.

Application of the μ cal-EDS to resolving analytical situations with severe peak overlap in conventional EDS spectrometry (e.g., Cu-L and Zn-L) was demonstrated. Long duration (minimum 1000s) measurements, necessary to accurately measure trace constituents ($C \leq 0.01$ mass fraction), were found to be subject to peak position and gain function instability. The instability results in degraded resolution by a factor of two or more. Division 837 researchers are currently working with NIST Boulder personnel to



understand the cryoelectronic circuitry to diagnose and attain more stable energy calibration.

Impact: The μ cal-EDS x-ray spectrometer potentially represents an extraordinary advancement in the microanalysis characterization of materials. The commercial development of this technology coupled with the measurement-science efforts of Div. 837 will directly impact many of NIST's customers involved in the areas of nanotechnology, electronics, materials science, failure analysis, and homeland security.

Future Plans: It is anticipated that after successful resolution of the μ cal-EDS problems attention will shift from the operational process to an extensive program of fundamental measurements in support of microanalysis needs, such as the application of low-voltage microanalysis to nano-scale characterization, accurate values of the relative peak heights within x-ray families, peak shifts due to chemical bonding, as well as direct application to materials chemistry problems.

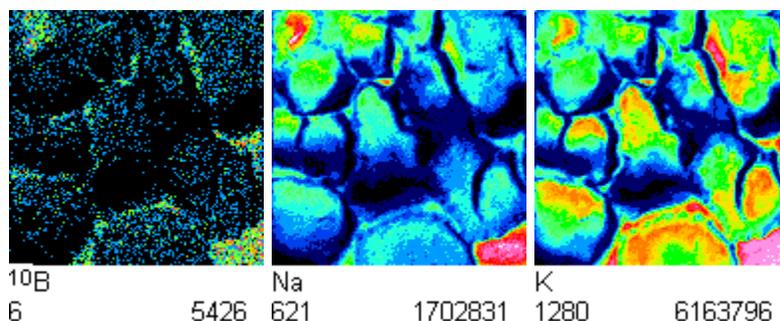
Localization of Boron Neutron Capture Chemotherapeutic Agents by Secondary Ion Mass Spectrometry

CSTL Program: Health and Medical Products/Services

Authors: S. Roberson, and G. Gillen (837); and S. Chandra (Cornell University)

Abstract: Glioblastoma multiforme is the most malignant form of brain cancer. Boron Neutron Capture Therapy (BNCT) has proven to be an effective treatment option for this form of cancer and provides a mechanism to destroy cancerous cells without injuring neighboring normal cells. The success of BNCT relies on the selective loading of boron in the tumor cells. This project evaluated the use of secondary ion mass spectrometry (SIMS) to image the location of isotopically tagged boronated compounds in T98G human glioblastoma cell cultures and to evaluate cell viability by means of the Na/K ratios. We have mapped the distributions of ^{10}B , Na, Mg, K and Ca in freeze-fractured cell cultures. This work has the potential to provide valuable information regarding the optimization of therapeutically useful dosages for ^{10}B -containing compounds. Future plans include localizing the chemotherapeutic agent by means of molecular secondary ion signals and exploring means to enhance the signals obtained.

Purpose: The purpose of this project was to use the high spatial resolution isotopic and molecular imaging capabilities of secondary ion mass spectrometry (SIMS) for the localization of isotopically tagged boronated compounds in tumor cell tissue cultures. There is significant interest in utilizing boron neutron capture therapy (BNCT) as a form of cancer radiation treatment that destroys cancer cells without injury to adjacent healthy tissue. BNCT has demonstrated effectiveness for treatment of several forms of cancer including glioblastoma and melanoma. Due to a lack of analytical techniques capable of measuring in-vivo ^{10}B concentrations (typically less than 100 $\mu\text{g/g}$ by weight) in tumors at the time of treatment, optimizing the therapeutic regimes has proven difficult. SIMS imaging is an ideal candidate for evaluating the distribution of BNCT drugs in tumor cell cultures and was used in this work to map Na, K, Mg, Ca distributions as well as the ^{10}B and ^{11}B isotopes at sub-cellular spatial resolution.



Major Accomplishments: One of the primary issues addressed in this work was the viability of the cell freeze-fracture preparation process and development of a method to identify undamaged cells. Cells cultures on silicon are rapidly frozen in liquid nitrogen to

maintain the in-vivo distribution of diffusible elements and the chemotherapeutic agent. If the cell is injured in this process, the plasma membrane becomes permeable to ion gradients. Cells will consequently lose intracellular potassium and gain extra-cellular sodium. Cell damage occurs frequently during the freezing process. This damage can invalidate the SIMS imaging experiments due to possible migration of the analyte molecules. It is critical that regions of undamaged cells be localized for analysis. We use the Na and K secondary ion image intensities as indicators of cell viability. The image above shows secondary ion images from a freeze-fractured specimen of a T98G human glioblastoma cell culture, containing ^{10}B enriched boronophenylalanine (BPA). A 25 keV Ga^+ primary ion was rastered over a $111\ \mu\text{m} \times 111\ \mu\text{m}$ area to acquire the images. Damaged cells show high levels of sodium and low levels potassium. The images above show expected ratios for a region containing healthy cells. A second major issue was to determine if sub-micron localization of the ^{10}B were possible at physiologically relevant concentration levels. The figure above also shows the ^{10}B distribution in the cells. Sufficient sensitivity is available to determine the distribution of the ^{10}B . ^{10}B appears to be distributed nearly homogeneously throughout the cells. We deduce that the more intense signals (brighter areas) that are seen on the periphery of the cells are due to an artifact of the SIMS experiment and do not reflect an actual concentration gradient. The origin of this artifact will be addressed in future work. Because of the low concentration of the boronophenylalanine, secondary ion counts for the ^{10}B are one to two orders of magnitude lower than for the matrix elements, Na and K. In order to increase the sensitivity of the analysis, further analyses are being conducted using an O_2^+ microbeam. A collaboration has also been initiated to develop a new high-brightness ion source for this application.

Impact: The success of BNCT relies on the selective loading of boron in the tumor cells. The results indicate that SIMS is ideally suited for assessing cell health and for the evaluation of BNCT drugs. The technique could be used to provide initial screening and evaluation of the efficacy of new boron therapeutic agents.

Future Plans: This preliminary work provided promising data on the feasibility of utilizing SIMS to determine the localization of boronated cancer chemotherapy drugs. In the future, we will concentrate our efforts on increasing elemental secondary ion signals. We are collaborating with a small company on the design of a high-brightness O_2^+ source for microbeam imaging on our magnetic sector instruments. Additional plans include mapping molecular secondary ion signals, locating sub-cellular structures, and quantifying the chemotherapeutic agents.

New Version of the NIST Electron Elastic-Scattering Cross-Section Database

CSTL Program: Industrial and Analytical Instruments and Services

Authors: *C.J. Powell, and A. Jablonski (Contractor); and F. Salvat (University of Barcelona, Spain)*

Abstract: Cross sections for the elastic scattering of electrons by atoms are needed for modeling the transport of electrons in materials by Monte Carlo simulations and other means. Such transport calculations are needed to improve the accuracy of surface analyses, bulk analyses, and thin-film analyses of inhomogeneous samples by the techniques of Auger-electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), electron-probe microanalysis (EPMA), and analytical electron microscopy (AEM). The cross sections are also needed for similar transport calculations in other applications including radiation dosimetry, radiation therapy, radiation processing, radiation protection, and electron-beam lithography.

A new version of the NIST Electron Elastic-Scattering Cross Section Database (SRD 64) was completed in FY2002 and is expected to be released in early FY2003. This version (Version 3.0) contains two major changes from Version 2.0. First, the cross sections and related data were calculated from a relativistic Dirac partial-wave analysis in which the potentials were obtained from Dirac-Hartree-Fock electron densities computed self-consistently. This potential is believed to be more reliable than the Thomas-Fermi-Dirac potential used previously. Second, the upper energy limit for the cross-section data has been extended from 20 keV to 300 keV. As a result, the database should be useful for a wider range of materials-characterization applications.

Purpose: To provide needed reference data for surface analyses by Auger-electron spectroscopy and X-ray photoelectron spectroscopy and for bulk and thin-film analyses by electron-probe microanalysis and analytical electron microscopy.

Major Accomplishments in FY2002: Version 3.0 of SRD 64 provides differential cross sections, total cross sections, transport cross sections, and phase shifts for the elastic scattering of electrons with energies from 50 eV to 300 keV (in steps of 1 eV) for atoms with atomic numbers from 1 to 96. These cross sections were computed with a more accurate atomic potential than that used for the data in Version 2.0 of this database.

Version 3.0 of SRD 64 has the following capabilities:

- Graphical display of differential elastic-scattering cross sections in different coordinate systems
- Graphical display of the dependence of transport cross sections on electron energy
- Display of numerical values of differential elastic-scattering cross sections, total elastic-scattering cross sections, and transport cross sections
- Creation of files containing differential elastic-scattering cross sections for specified elements, energies and coordinates

- Creation of files containing plots of differential elastic-scattering cross sections versus scattering angle for one or more elements or for one or more electron energies
- Creation of files containing phase shifts for specified elements and for energies up to 20,000 eV
- Creation of files containing transport cross sections for specified elements and energies
- Creation of random number generators providing the polar scattering angles to be used in Monte Carlo simulations of electron transport in solids; and
- Tests of the random number generators

Impact: It will be possible to make more accurate simulations of electron transport to provide more reliable analyses of inhomogeneous specimens by AES, XPS, EPMA, and AEM. There will be similar benefits for other applications such as radiation dosimetry and electron-beam lithography.

Future Plans: A review article is in preparation that will examine the differences in differential cross sections from Versions 2.0 and 3.0 of SRD 64 and the consequential effects of these differences on certain quantities derived from analyses made with these cross sections. Particular attention is being given to the determination of electron inelastic mean free paths by elastic-peak electron spectroscopy and to mean electron escape depths for surface analyses by AES and XPS.

Chemical Imaging of Polymer Blends with Confocal Raman Microscopy

CSTL Program: Industrial and Analytical Instruments and Services

Author: C.A. Michaels

Abstract: Confocal Raman microscopy has been used to study spatial variations in chemical composition and crystallinity for polymer blend films of interest to the industrial members of the NIST/industry polymer interface consortium. This chemical imaging technique yields data sets consisting of Raman spectra at each (x,y) sample coordinate, with diffraction limited lateral resolution ($\sim 0.5 \mu\text{m}$) and excellent depth discrimination ($\sim 5 \mu\text{m}$). The chemical selectivity of Raman spectroscopy has been exploited to characterize the spatial distribution of a high value fluoropolymer in an acrylic resin film used as a protective coating for metal substrates in building applications. This technique has also been used to examine the relationship between thermal history and film morphology through spectral characterization of the level and spatial variation in crystallinity for polyethylene (PE) blends. Future efforts will focus on characterization of the chemical microstructure and morphology of these materials as a function of composition and thermal processing conditions.

Purpose: To study spatial variations in chemical composition for polymer blend samples of interest to our industrial collaborators (Dow Chemical, PPG Industries, Visteon, and MTS Systems) in the NIST/industry consortium on the *Characterization and Modeling of the Interfaces and Interphases of Polymeric Materials and Systems*. Confocal Raman microscopy is used to image the spatial distribution of polyvinylidene fluoride (PVDF) in PVDF/acrylic resin blend films employed as a coating formulation for architectural steel and aluminum. Semicrystalline polyolefin blend films are also studied with confocal Raman microscopy wherein spectral signatures of crystallinity are used to assess both the degree of crystallinity and its spatial variation as a function of thermal processing.

Major Accomplishments : Confocal Raman microscopy has been used to study the spatial distribution of fluoropolymer in blend films provided by PPG, consisting of PVDF and the acrylic resin, PMMA-co-PEA. The fluoropolymer provides this material with the chemical resistance to attain remarkable performance in weathering tests over several decades, whereas the resin is used to reduce cost and promote substrate adhesion. Thus the relationship between functionality and composition is of significant interest, and it is expected that measurements of the chemical microstructure of the film will yield insight into this relationship. The spatial distribution of film components in the direction normal to the substrate surface is

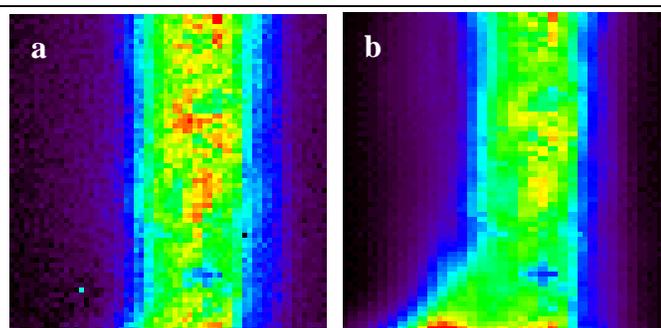
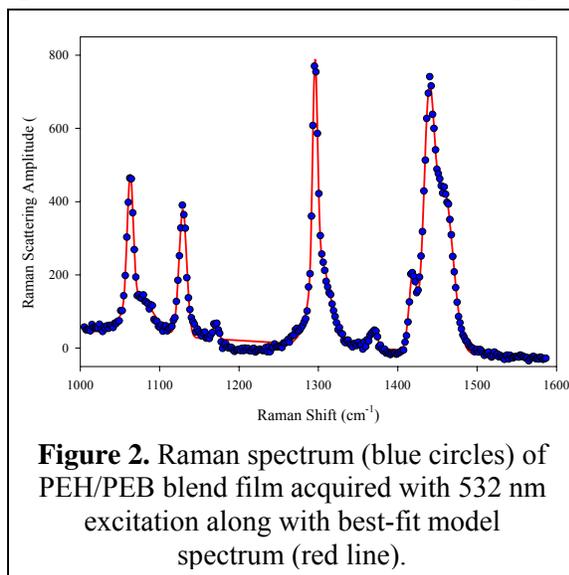


Figure 1 (a) $64 \times 64 \mu\text{m}$ intensity map of CF_2 Raman band of PVDF/PMMA-co-PEA film cross section. The film/substrate (air) interface is on the right (left) side of the film cross section. (b) Fluorescence intensity map acquired simultaneously with (a).

of particular importance. Raman spectra at 785 nm excitation of the film/substrate and film/air interfaces of a blend film (50/50 mass ratio) suggest a preferential depletion of PVDF at the substrate interface. However, images of film cross sections, as shown in Figure 1(a), where the intensity of the CF_2 stretching band at 799 cm^{-1} has been plotted, reveal no obvious PVDF gradient between the film surfaces. The markedly different surface and air interface spectra, coupled with the lack of a strong CF_2 gradient in the film cross sections, suggest that only a thin, surface depletion layer exists at the substrate interface. Figure 1(b) is a fluorescence image of the film cross section recorded simultaneously with that shown in Figure 1(a), the difference in the images clearly demonstrating the chemical selectivity of Raman imaging. The sample preparation method used here is expected to result in significant surface roughness and measurements designed to assess its impact on the spectral maps are ongoing.

The thermal processing of polyolefin blends drives the interplay between the kinetic processes of liquid-liquid phase separation and crystallization that ultimately controls sample morphology. We have been exploring the use of confocal Raman microscopy as a tool for assessing the degree of crystalline content and its spatial variation in blends of polyethylene-co-hexene (PEH) and polyethylene-co-butene (PEB) samples as a function of their thermal history and composition. Figure 2 shows a typical Raman spectrum (blue circles) of a PEH/PEB blend film at 532 nm excitation along with a best fit model spectrum consisting of bands due to crystalline and amorphous phases.

The CH_2 bending vibration at 1418 cm^{-1} results from a factor group splitting due to the crystal field of the orthorhombic crystal structure and is a clean signature of crystallinity in polyethylenes. Mapping of this band intensity (normalized to an internal standard) yields a crystallinity image with diffraction limited lateral resolution and depth resolution set by the confocal parameter of the collection optics, typically on the order of $5\text{ }\mu\text{m}$. Current work is focused on samples for which the thermal processing has been optimized for production of crystallites with $1\text{-}20\text{ }\mu\text{m}$ diameters.



Impact: This work was recently presented at a consortium review meeting, held at PPG Industries Coatings R&D Center in Allison Park, PA on September 11th and 12th. A manuscript entitled, "Surface and interface properties of PVDF/acrylic copolymer blends before and after UV exposure," that includes initial confocal Raman data along with other work of the NIST technical team on the PVDF system, will appear in the *2002 Proceedings of the International Coatings Exposition*. Efforts to facilitate the transfer of confocal Raman chemical imaging technology to other industrial partners (Exxon-Mobil) through sample evaluation and interaction with visiting scientists are ongoing.

Future Plans: Application of this chemical imaging technique to new sample systems of interest will continue in collaboration with our consortium partners. Ongoing measurements are aimed at mapping the PVDF distribution in cross-sectional films obtained by various sample preparation methods, including fracture, microtomy, and polishing. These measurements will be extended to PVDF/PMMA-co-PEA blend films with varying composition and thermal processing history. The crystallinity mapping technique will continue for PE blend samples and extended to the study of polypropylene blend films provided by Dow Chemical.

Spectroscopic Study of the Structure of Oligo-phenylene-ethynylene Monolayers with Molecular Electronics Implications

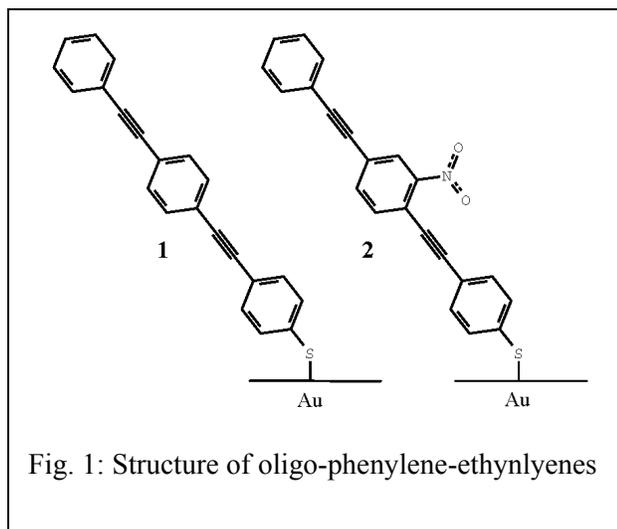
CSTL Program: Microelectronics

Authors: C.S.-C. Yang, P.T. Wilson, and L.J. Richter (837); R.D. Van Zee (836); J.J. Stapleton, and D.L. Allara (Pennsylvania State University)

Abstract: Intense interest has recently been focused on the possibility of using chemical self assembly of appropriately chosen molecules to build electronic devices in a bottom-up fashion. This could lead to improvements in cost and device density over traditional semiconductor fabrication techniques. Simple electrical behavior such as conductance, rectification, and negative differential resistance (NDR) has been demonstrated in devices with a single monolayer of active molecules. Insights into the mechanisms underlying the observed molecular electronics phenomena have been limited due to the complete absence of spectroscopic tools appropriate to the study of the small molecular contacts. NIST, in collaboration with PSU, is exploring the potential of using advanced nonlinear optical probes to characterize the structure of electrically active molecular films. The structure of monolayer films has successfully been characterized with tools of adequate spatial and temporal resolution to enable characterization of electronically perturbed states.

Purpose: Oligo-phenylene-ethynylene molecules represent an interesting class of electronically active species. When assembled in nanoscale junctions,¹ molecule **1** is a conductor under forward bias that exhibits rectification (diode-like behavior). Molecule **2** exhibits NDR (a bias dependent conductance switch). A number of models have been proposed to explain the NDR behavior of **2**. Validation of these models has been hampered by the inability of conventional spectroscopic tools to probe the structure of the film in

functional devices that have only a few μm^2 area. Vibrationally-resolved sum-frequency generation (VR-SFG) is a non-linear spectroscopy that is capable of determining the molecular structure and orientation of monolayer films. It has both a time-resolution (~ 100 fs) and spatial resolution (~ 50 μm dia) that will enable measurements in functioning devices. However, no VR-SFG studies have been performed on oligo-phenylene-ethynylenes so the spectroscopic constants necessary for the interpretation of the spectra are unknown.



¹ J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, Science 286 1550 (1999)

Major Accomplishments : High quality monolayers of 1 and 2 were formed on Au substrates at PSU. VR-SFG spectra were recorded over the spectral range 1000 to 3200 cm^{-1} on both molecules at NIST. Shown in Fig. 2 are spectra recorded for two combinations of the polarizations of the three optical beams: ppp and ssp. The features at $\sim 1500 \text{ cm}^{-1}$ and 1600 cm^{-1} for both molecules are due to vibrations of the 3 phenyl rings. The feature at $\sim 1540 \text{ cm}^{-1}$ in 2 is due to the NO_2 group. Also shown in Fig. 2 are spectra predicted based on *ab initio* calculations of the nonlinear line strengths of the two molecules. The *ab initio* spectra are in good agreement with the experimental spectra. The ratios of the resonance features for the two conditions can be used to determine the orientation of the molecule. Preliminary analysis of both molecules indicate they are tilted away from the surface normal by about 35° , as indicated in Fig. 1.

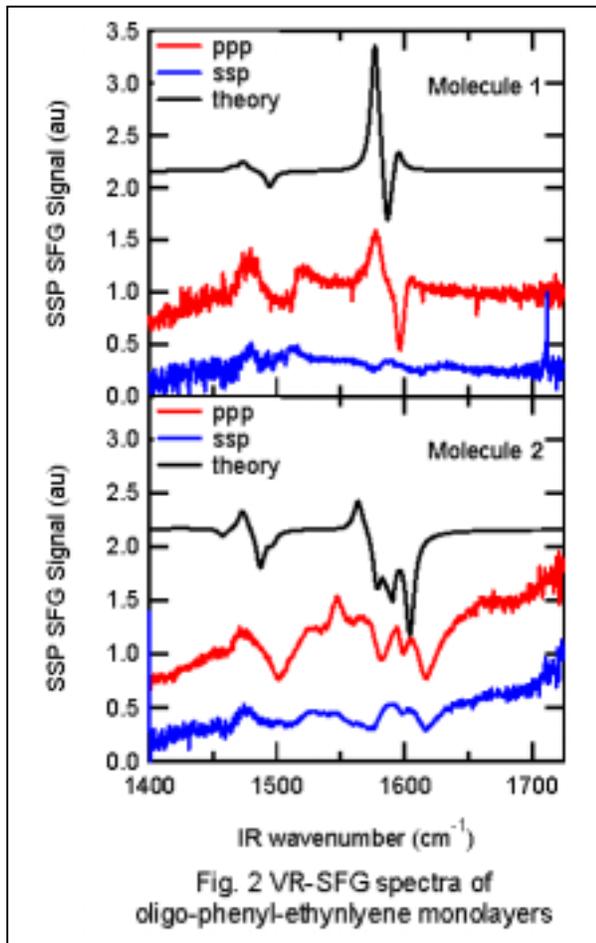


Fig. 2 VR-SFG spectra of oligo-phenyl-ethynylene monolayers

Impact: Our understanding of the structure of dense monolayers of the oligo-phenylene-ethynlyenes is maturing. The VR-SFG measurements are consistent with recent IR measurements of the tilt of the molecules,² and the similarity of the film structure for 1 and 2. This data is also consistent with *ab initio* calculations of the structure of isolated adsorbed molecules.³

Future Plans: Coupling between the electronic and vibrational degrees of freedom of the oligo-phenylene-ethynlyenes will be characterized by performing VR-SFG measurements of the molecules following optical excitation and in the presence of an electric field established by a transparent electrode. These measurements will provide an indication of the structural changes that occur as the conductance state of the molecule is switched.

² J.J. Stapleton, et al. in preparation.

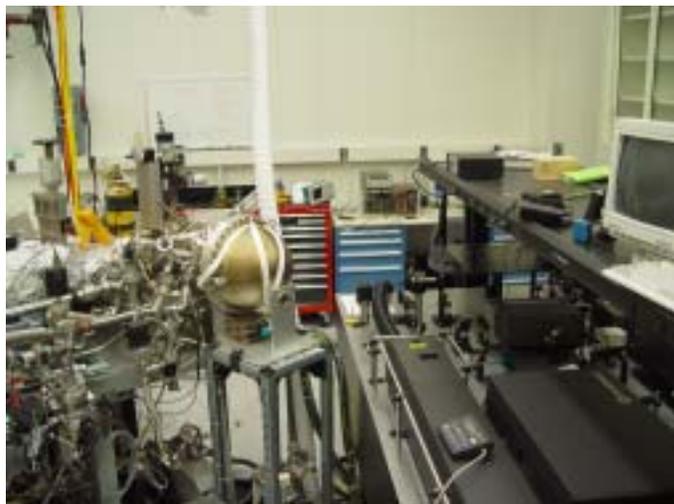
³ Carlos Gonzalez, private communication.

Electronic Structure and Transport in Model Molecular Electronic Systems

CSTL Program: Microelectronics

Authors: *J.D. Batteas, and S.W. Robey (837); and R.D. Van Zee, and C.D. Zangmeister (836)*

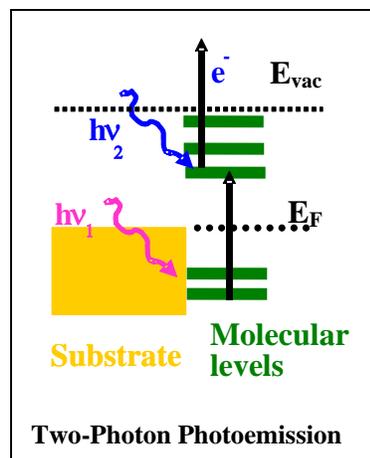
Abstract: The drive to increase electronic device performance, with the associated push to ever smaller device dimensions, has lead industry observers to conclude that silicon-based technology will reach a point of diminishing gains in the near future. This, in turn, has generated interest in alternatives technologies based, for instance, on single-electron devices and molecular components. It is hoped that the tremendous flexibility available with organic synthetic chemistry and self-assembly techniques can be harnessed to produce non-linear devices analogous to silicon-based diodes and transistors, but comprised of single or small numbers of molecules.



The CSTL effort in molecular electronics is developing a battery of techniques that will provide necessary information on electronic structure and electron transport in candidate molecular electronic systems. The methods being used include two-photon photoemission, which accesses unoccupied electronic levels and tracks electron relaxation effects, and scanned probed techniques, which can characterize electron transport down to the single molecule level.

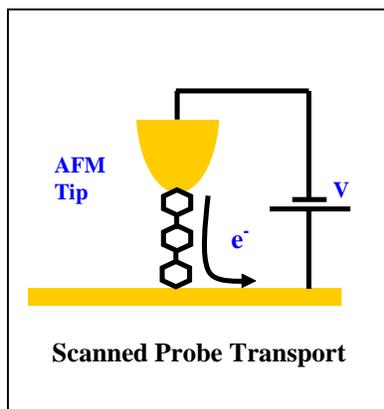
Purpose: This work will develop measurement techniques and expertise necessary to understand electronic structure and dynamics in mesoscopic systems comprised of organic thin films and small molecular aggregates. The overall goal is to provide information that, when coupled with theoretical input, will help to illuminate the physical mechanisms that produce the useful, non-linear effects observed in molecular electronics device-prototypes. This information is also required to develop measurement standards and test protocols for such devices.

Major Accomplishments: This has primarily been a year of validating the performance of laboratory instrumentation against well-characterized systems. An ultrahigh vacuum analysis system was assembled and coupled to a femtosecond Ti:sapphire laser for studies of electronic structure using two-photon photoemission. A



scanned-probe system was purchased and a new hire was brought on to lead investigations of the structure and transport properties in model molecular electronics systems. Preliminary studies of d-c transport through small numbers of conjugated molecules were also begun.

Impact: This project is poised to begin providing results that will lead to a more complete understanding of electronic structure and transport effects in molecular electronic systems. These results will benefit the development not only of potential molecular electronics applications, but will also find use in current technologies using organic molecules in electronic applications such as light emitting diodes and field effect transistors.



Future Plans: In upcoming years, we will study the electronic structure and conduction properties of a series of molecules from the oligio-(phenyl-ethnyl) family of molecules. These experiments will include conventional and multi-photon electron spectroscopies conducted on films of these molecules. The scanned-probe instrument will be used to study the conduction properties of small aggregates of conductive molecules. The structural and conduction properties of these pads will be compared to those of large areas films. The results from these experiments will be compared to theoretical models develop by our collaborators in the Physical and Chemical Properties Division and to the performance of device-prototypes fabricated and tested by our collaborators in the Semiconductor Electronics Division.

Fabrication of the Building Blocks of Multifunctional Nanoscale Sensors

CSTL Program: Industrial and Analytical Instruments and Services

Authors: *R.M. Hernández, and S.J. Stranick*

Abstract: Nanowires with integrated chemical and biochemical species have been fabricated with the goal of having these structures serve as the building blocks in multifunctional nanosensors. The use of bottom-up, nanoscale synthesis allows the controlled incorporation of a variety of recognition elements in segments of polymeric matrices within individual nanowires, engineered to meet specific sensing requirements. The high concentration of affinity elements contained in the nanowire volume, and the individual sensing capabilities of each chemically selective sequence are some of the unique features of this system. In addition, optical signatures can be carefully incorporated to allow identification of diverse analytes. Moreover, because this design provides for electronic transduction by employing conducting and semiconducting materials, these nanostructures could also produce a characteristic electronic signature for each type of affinity interaction. These transduction effects are evaluated using segmented metal/polymer/metal nanowires.

Purpose: The purpose of this project is to develop novel nanoparticle and nanowire technologies as potential building blocks for next-generation analytical sensors. Our model system consists of nanowires with built-in affinity elements that impart each particle with a unique sensing capability. These nanowires can be interfaced independently with electrical signal transducers to provide increased selectivity and sensitivity.

Major Accomplishments: Nanowires composed of metal and conducting polymer segments have been successfully fabricated using chemical and electrochemical synthesis inside the preformed nanoscale pores of anodic alumina membranes. Figure 1 shows a 300 nm diameter, 5 μm long nanowire composed of alternating gold (bright) and polypyrrole (PPY) (dark) segments. Biochemical selectivity is imparted to the PPY segment by physical entrapment of antibodies, enzymes, and other receptors during electrochemical synthesis. In our work, the strong binding affinity between avidin and biotin is used to demonstrate biochemical selectivity as well as to access the impact of synthesis conditions on biological activity. In this experiment, the presence of entrapped, fluorescently labeled avidin in PPY was verified by fluorescence microscopy, and it was found that a PPY matrix can support electrical transduction without causing a denaturing of avidin or a loss of bioactivity in avidin: a necessary condition for the generation of conductance-based sensors. A clear

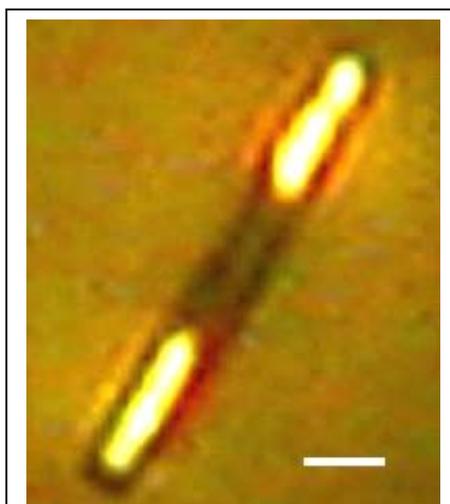


Figure 1: Optical micrograph of a 300 nm diameter nanowire comprised of Au outer segments and a polypyrrole inner segment. Scale bar is 1 μm .

advantage of this entrapment process is that direct coupling or binding of the chemical/biological species is not required for immobilization/incorporation, *i.e.* a diverse array of chemical and biological analytes can be incorporated based on their ability to sense and rather than on their ability to bind.

Impact: Nanowire systems will provide multiple options for sensor design with additional sampling and measurement capabilities made possible by the miniaturization and integration of these components. Because any biological elements can theoretically interface with any of a wide variety of signal transducers (e.g., optical, electrochemical, thermal, or acoustic), the potential range of devices and techniques can be substantial. This methodology will provide an inexpensive and straightforward approach to the synthesis of sensing devices with multiple functionalities that can be integrated to current solid-state technology.

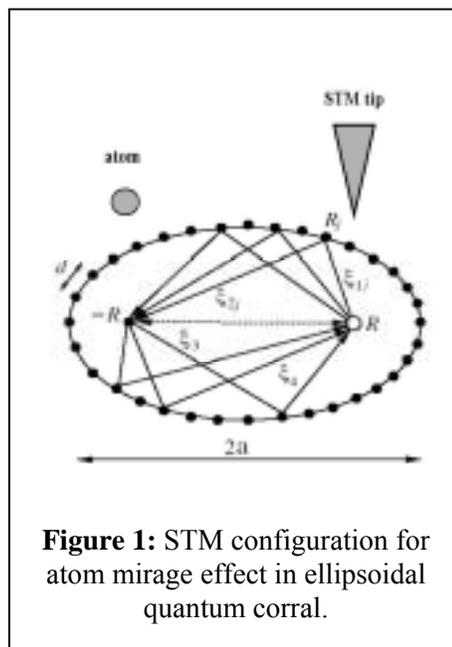
Future Plans: Our preliminary studies focused on the synthesis of nanowires composed of gold and polypyrrole segments. These methodologies will be employed to generate analogous materials that expand on the chemical, electrical, and biological properties of nanowire systems. In addition, we are working on strategies for the nano-manipulation and directed assembly of nanowires, which is essential for the controlled integrations of discrete nano-devices into mesoscale and macroscale sensor arrays.

Quantum Mirages in STM of Surface Nanostructures

CSTL Program: Industrial and Analytical Instruments and Services

Author: J.W. Gadzuk

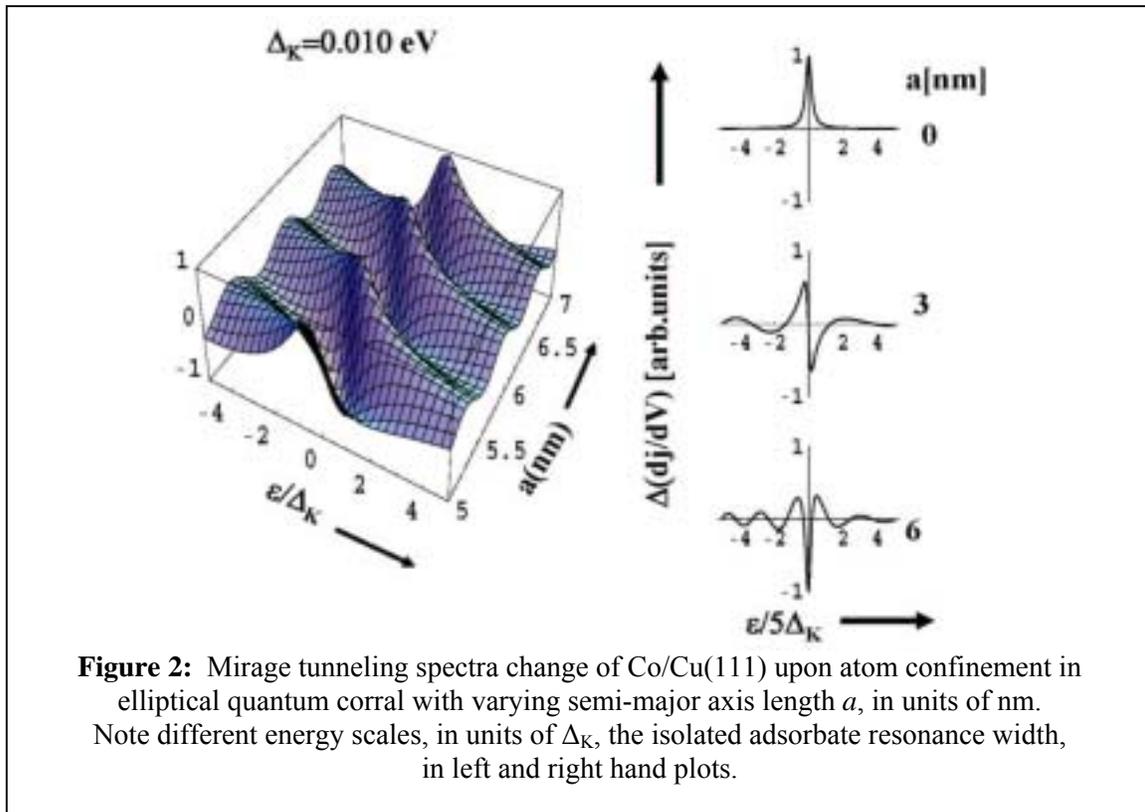
Abstract: Scanning tunneling microscopy/spectroscopy of atoms adsorbed upon metal surfaces provides intriguing visual images and spectroscopic signatures in the form of chemical-environment-specific lineshapes. STM studies have demonstrated the ability of suitable two-dimensional nanostructures (such as “quantum corrals”) to influence the surface electron transport that is part of the total STM process. In a well known paradigm, an elliptical arrangement of adsorbed atoms gives rise to an apparent enhanced electronic communication between points on the surface which are near the two elliptical foci. Theory for the total process of tip-to-corrals state tunneling, focus-to-focus transport via (corrals) surface states, and adsorbate resonance scattering has been developed. Observable lineshapes have been predicted that illustrate the potential utility of tunneling spectroscopy for obtaining unique, atomic scale understanding of the role of nanostructure size, shape, and chemical composition on both surface transport processes and also on the measurement methodologies required to probe such systems. This has presented unusual challenges since all the characteristic energies [resonance position and width, vibrational, relaxation, and quantum corral] are of comparable magnitude in realistic experimental STM studies.



Purpose: Atomic-scale probes such as scanning tunneling microscopy/spectroscopy are the *sine qua non* for characterization of “chemically interesting” surface nanostructures which are the fundamental building blocks upon which the nanotechnology revolution is based. A significant purpose of this project is to provide not only a motivation and challenge, but more importantly, the necessary theoretical tools for guiding and interpreting experimental STM studies on the quantum behavior of atoms and/or molecules confined within surface nanostructures.

Major Accomplishments: Theory has been developed for predicting the scanning tunneling spectrum or resonance signature of atoms/molecules adsorbed on surfaces, both as isolated entities as well as quantum-confined within surface nanostructures such as the elliptical corral which provides the ideal realization for concept testing. The basic 3-step process depicted in Fig.1 consists of STM-to-surface tunneling at R , the unoccupied elliptical focus, followed by focus-to-focus surface electron transport via constructively-interfering paths involving scattering from the constituent atoms of the ellipse/nanostructure [this is the key to the generation of the quantum “mirage”], and

finally resonance scattering/sensing of the “miraged” atom occupying the focus at $-R$. Our analytic solutions for each of these independent steps have enabled determination of the corral-induced change of the tunneling spectra or differential conductivity of the tip-to-surface configuration. As an example, the sample spectra shown in Fig.2, with system parameters relevant to Co on Cu(111), demonstrate the extreme path-length sensitivity of the adsorbate spectra on the corral size, as conveyed by the value of a , the semi-major axis length. The individual spectra on the right show both evolving oscillatory structure due to the size-dependent quantum bound states of the corral as well as complete change in the character of the central lineshape. The contour plot on the left nicely illustrates the size-dependent spectral changes over a continuous range of experimentally-important ellipse sizes. Clearly a wealth of potentially useful information on the influence of nanostructures on atomic systems is inherent in measurements of this type.



Impact: This theory makes more feasible the use of scanning tunneling probes for interpretable quantitative identification and characterization of atomic scale chemical systems which include surface nanostructures.

Future Plans: We hope to consider other nanostructures and probed species, and to include polaron/vibrational mirageing, if our preliminary studies prove this to be potentially useful. It remains to be seen whether we can exploit rather than be burdened by this extreme tunneling-spectroscopy-nanosensitivity.

Total Carbon Determination In Buffalo River Sediment Using Isotope Dilution Mass Spectrometry

CSTL Program: Environmental Technologies and Services

Authors: *D. Klinedinst, and M. Verkouteren (837); and K. Revesz (USGS, Reston, VA)*

Abstract: Accurate measurements of carbon concentration are of great relevance to many sectors of the US economy, and carbon is rapidly becoming a global commodity due to its tremendous relevance in global climate change. Unfortunately, there are no SRMs with *certified* carbon concentration values. While non-certified values exist, determination of these values have most recently relied on operationally dependent measurement techniques that are frequently referenced to standards with mismatched matrices. Isotope dilution mass spectrometry (IDMS) is a well-known and “absolute” technique for determining the concentration of a particular analyte. Because IDMS concentration measurements depend entirely on sample gravimetry and the isotope ratio measurements of a sample, a labeled spike material and an equilibrated mixture of the two, the technique is especially applicable for materials with complex matrices. NIST RM 8704, the Buffalo River Sediment (BRS) is a natural, complex matrix material, and serves as a suitable benchmark for the evaluation of IDMS performance with respect to the quantitative determination of carbon concentration. The carbon determinations for BRS of both the SRM and RM were quite comparable, and thus provided a solid reference value with which the IDMS technique could be evaluated.

Purpose: To develop measurement protocols for the determination of total carbon using IDMS and to evaluate the applicability of this technique for the certification of carbon in NIST SRMs. This capability is critical for meeting National challenges in carbon sequestration, environmental “health” and to provide accurate benchmarking materials for many industrial sectors concerned with the carbon content of feed stocks and process residues.

Major Accomplishments: RM 8704, the Buffalo River Sediment (BRS) is a natural, complex matrix material, and serves as a suitable benchmark for the evaluation of IDMS performance with respect to the quantitative determination of carbon concentration. The initial bottling of BRS (SRM 2704) had a certified carbon value determined via coulometry and/or inert gas fusion/IR detection. Upon reissue of the BRS, these methods were no longer in use thus updated carbon values were no longer designated “certified”. Nevertheless, the carbon determinations of both the SRM and RM were quite comparable and thus provided a solid reference value with which the IDMS technique could be evaluated. Protocols developed for the determination of the carbon concentration in BRS using IDMS consisted of the quantitative combustion of the sample materials to CO₂ at 900 °C in a sealed quartz tube. Subsequently CO₂ was liberated within a closed vacuum manifold, distilled to remove water, cryogenically transferred for manometric quantification, and storage. Isotopic ratios were measured using two isotope ratio mass spectrometry techniques: dual inlet/IRMS (NIST) and Gas Chromatography/IRMS (USGS). The combined NIST/USGS data indicated a relative difference between the existing RM 8704 carbon reference value and the new NIST result

of 1.6%. The resulting carbon values are consistent and comparable, but these values have uncertainty levels indicating that further refinement of the method is necessary.

Impact: When applied to certify carbon in NIST Standard Reference Materials, IDMS will provide accurate abundance values in a variety of important matrices, including sediments, soils, particulate matter and fuels. Information regarding the amount of carbon is a potentially important metric in a number of arenas, including the development and validation of carbon sequestration methods in soils, the establishment of carbon “credits” that offset greenhouse gas emissions and the determination of the price of high-volume commodities.

Future Plans: This work indicates that for IDMS to be a viable technique for the quantitative determination of carbon concentration, further optimization of the method is required, specifically with respect to the minimization of water and N₂O interferences, with the goal of improving overall uncertainties to < 0.15%. Analogous to carbon, NIST has also lost the ability to certify nitrogen. Because carbon and nitrogen IDMS protocols are quite similar, methods could also be developed for total nitrogen determination. Moreover, the IDMS method had broad applicability and could be easily extended other applications, notably, the study of isotopic variations for forensic applications.

Gravimetric Results of a Fine Particulate Carbonaceous Reference Material on Quartz-Fiber Filter (SRM Project 2784)

CSTL Program: Environmental Technologies and Services

Authors: G. Klouda; and J. Filliben (898)

Abstract: Gravimetric results have been compiled and analyzed for the production of RM 2784 urban dust on quartz-fiber filters, including process and control blank filters. The distribution of PM loadings and relationships with respect to chamber position, chamber and batch was variable but expected. The average mass loading and standard deviation for 2231 filters is $1064 \pm 414 \mu\text{g PM}_{2.5}$ per filter. Given the relative standard deviation of mass loading of 39 %, filters identified for a round-robin exercise will be randomly selected from eight stratified mass-loading intervals. The design will be balanced with a strong emphasis on replication and true round-robin sampling. Beyond the need to assign values of elemental carbon (EC), organic carbon (OC) and total carbon (TC) for each method, the results of this exercise are expected to yield information regarding possible mass interval effects, within-filter homogeneity, and filter-to-filter homogeneity. RM 2784 will provide the means to intercompare methods for the measurement of elemental carbon in particulate matter (PM).

Purpose: To determine mass loadings for each individual filter produced by a particle resuspension system. RM 2784 has been designed and produced especially for the seven EPA “Supersites” that are monitoring fine airborne PM throughout the U.S.

Major Accomplishments: A randomization plan was designed to set protocols for loading and handling of the filters, and the production of process blank and control blank filters. The distribution of PM loadings and relationships with respect to chamber position, chamber and batch was variable: average mass loading and standard deviation for 2231 filters was $1064 \pm 414 \mu\text{g PM}_{2.5}$ per filter with a range of $2763 \mu\text{g}$ and a minimum and maximum of $92 \mu\text{g}$ and $2855 \mu\text{g}$, respectively. Given the relative standard deviation of mass loading of 39 %, filters identified for a round-robin exercise to assign values for EC, OC and TC will be randomly selected from eight stratified mass-loading intervals. Two of the most widely used thermal-optical methods, STN and IMPROVE, will be the focus with two of the most qualified laboratories representing each method. The design will be balanced with a strong emphasis on replication and true



Figure 1. 55 of 2231 filter-based PM_{2.5} standard materials. Gravimetry quantified the variation in loading that is observed here. An intercomparison exercise was designed to utilize accepted thermal-optical analysis protocols to explore possible loading effects.

round-robin sampling. Beyond the need to assign values of EC, OC and TC for each method, the results of this exercise are expected to yield information regarding possible mass interval effects, within-filter homogeneity, and filter-to-filter homogeneity.

Impact: RM 2784 will provide the means to intercompare methods and laboratories for the measurement of elemental carbon in PM. Use of this RM will determine the level of agreement between sites and establish traceability to stated references based on thermal-optical techniques.

Future Plans: We will finish SRM Project 2784 early in FY03 with the completion of the intercomparison exercise and assignment of EC/TC values based upon accepted measurement protocols. A website will be used to disseminate updated value assignments as further information becomes available.

Chemometric optimization of thermal-optical analysis in determining black carbon in atmospheric PM2.5

CSTL Program: Environmental Technologies and Services

Authors: J.M. Conny, D.B. Klinedinst, S.A. Wight, and J.L. Paulsen

Abstract: Atmospheric black carbon (BC), a ubiquitous component in fine (<2.5 micrometer diameter) particulate matter (PM2.5), is responsible for most of the uncertainty in climate change prediction. The chemical, physical, and morphological complexity of aerosol BC presents major problems in assuring measurement accuracy. PM2.5 metrology including BC accuracy is also a major concern of industrial leaders currently addressing the new EPA PM2.5 emissions standard. Methods based on thermal-optical analysis (TOA) are widely used for ambient air samples; however, different TOA thermal desorption protocols result in wide BC to total carbon (BC/TC) variation. We created three surface models of the following response variables from TOA: BC/TC, maximum laser attenuation in the He phase (L_{max}), and laser attenuation at the end of the He phase (L_{He4}). A two-level central-composite factorial design comprised of four factors considered the temperatures and durations of all desorption steps in TOA's inert (He) phase and the initial step in TOA's oxidizing (O₂-He) phase. The L_{max} surface was used to optimize the production of pyrolyzed organic carbon (OC char) in the He phase. Unpyrolyzed OC is measured as native BC, causing a positive bias. The L_{He4} surface was used to minimize the loss of char in the He phase, which served as a surrogate indicator for loss of native BC in the He phase, a source of negative bias. The intersection at the L_{max} and L_{He4} surface maxima revealed conditions that minimize potential biases, leading to an optimized thermal desorption protocol. ESEM images were used to better understand changes in particle population morphology during the TOA process. This quantitative map of the TOA response surface will help scientists to derive the most appropriate instrumental conditions for accurately measuring BC by TOA.

Purpose: To improve understanding of the key operational variables in thermal-optical analysis (TOA) by a systematic and repeatable chemometric approach. This is needed by the black carbon measurement community to improve intercomparability and interpretation of results based on measurement accuracy.

Major Accomplishments: We created three surface models of the following response variables: BC/TC, maximum laser attenuation in the He phase (L_{max}), and maximum laser attenuation at the end of the He phase (L_{He4}). A two-level central-composite factorial design comprised of four factors considered the temperatures

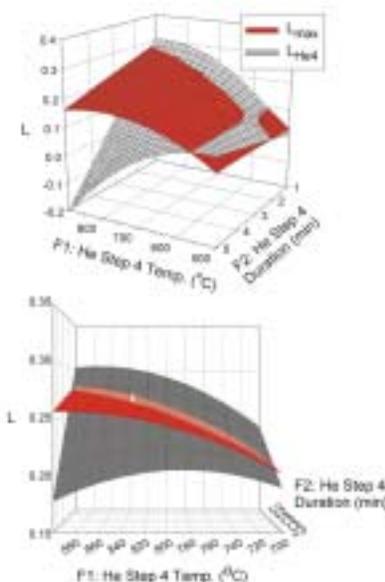


Figure 1. TOA response surface maps; lower map is rotated hi-res view of upper map.

and duration of all desorption steps in TOA's inert (He) phase and the initial step in TOA's oxidizing (O₂-He) phase. The L_{\max} surface was used to optimize the production of pyrolyzed organic carbon (OC char) in the He phase. Unpyrolyzed OC is measured as native BC, causing a positive bias. ESEM images were used to better understand changes in particle population morphology during the TOA process and to qualitatively assess the positive artifact.

The L_{He4} surface was used to minimize the loss of char in the He phase, which served as a surrogate indicator for the loss of native BC in the He phase, a source of negative bias. The intersection between the L_{\max} and L_{He4} surfaces at their maxima revealed conditions that minimize potential biases, leading to an optimized thermal desorption protocol. Our data suggest the following operating conditions when TOA is operated in the fixed-step-duration, laser-transmission mode (i.e., TOT): step 1 in He, 190 °C for 60 s; step 2 in He, 365 °C for 60 s; step 3 in He, 610 °C for 60 s; step 4 in He, 835 °C for 72 s. For steps 1-4 in O₂-He, our data suggest using 550 °C for 180 s, 700 °C for 60 s, 850 °C for 60 s, and 900 °C for 90 s.

Impact: This quantitative map of the TOA response surface will help scientists to derive the most appropriate instrumental conditions for accurately measuring BC by TOA. Due to the importance of TOA for assessing public health risk from atmospheric BC exposure, accuracy in BC by TOA may then help scientists find consensus on a more robust definition of BC.

Future Plans: We plan to apply these chemometric techniques to thermal-optical analysis of several U.S. regional PM_{2.5} samples. This will help to fine-tune the optimized thermal desorption protocol from this work, differentiate it if necessary for different types of ambient air samples, and validate robust TOA operational protocols.

Characterization of the Morphology of Faceted Nanoparticles by Transmission Electron Microscopy

CSTL Program: Technologies for Future Measurements and Standards

Authors: *S. Turner, and D.S. Bright*

Abstract: Characterization of the morphology of faceted nanoparticles is important in a variety of applications. The morphology controls the abundance, chemical composition and atomic arrangement of the particle surface and therefore controls the availability and activity of specific chemical sites on nanoparticles. For example, different crystallographic facets in catalysts have different efficiencies for promoting reactions. In pigment particles, certain morphologies are more desirable for the durability of paint. In the astrobiological field, considerable effort has gone into the characterization of faceted magnetite particles formed by some types of bacteria as markers for extraterrestrial life. Detailed knowledge of particle morphology can be critical to the chemical analysis of nanoparticles and to the increasing range of nanoparticle industry applications.

Characterization of faceting by transmission electron microscopy (TEM) is challenging because a TEM image is a two-dimensional projection of material. In this work, the application of a double-tilt rotation holder to improved manipulation of particles is tested and a method for morphology modeling developed. It is shown that by using this holder it is possible to orient a crystallographic direction of interest in a particle along a sample holder axis. A series of images is then collected and measurements of the dimensions made by using tools in a NIST-developed Lispix program. Possible models for the particle faceting are developed using commercially available SHAPE software. Comparisons of the experimental measurements to dimensions determined for different models of the morphology are then made to determine the best model for the particle morphology.

Purpose: To test the applicability of a double-tilt holder to improved characterization of the morphology of faceted nanoparticles.

Major Accomplishments: It was established that it is possible to align crystallographic directions of interest in a particle with TEM holder tilt axes using the double-tilt, rotation holder. This allows for a more systematic approach to testing models of morphology of faceted particles. This complex, 6-axis, motion control for three dimensional morphology is difficult, but for the first time allows large portions of both real-morphological and reciprocal crystallographic space to be explored and characterized

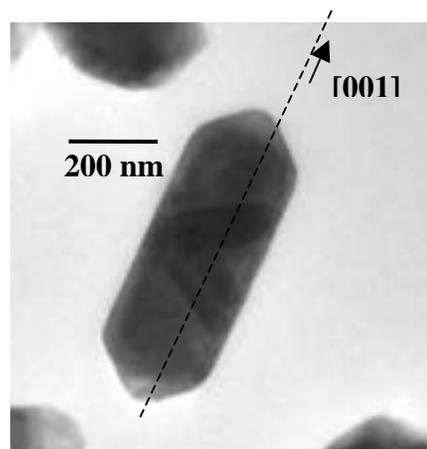


Fig. 1 Faceted rutile (TiO_2) pigment particle oriented so that c axis (arrow) and projection of holder rod axis (dashed line) are aligned. Tilting around axis allows for improved morphology determination.

accurately. We have related in three dimensions the morphologic facets with crystallographic planes using electron diffraction and the 6-axis stage.

Impact: The potential impact of this work is in improved morphology characterization of catalysts, paint pigment particles and other particles of industrial interest. The morphology controls the abundance, chemical composition and atomic arrangement of the particle surface and therefore controls the availability and activity of specific chemical sites on nanoparticles. Morphological effects on the chemical analysis of particles are well known as a major source of uncertainty ... frequently causing bias of greater than 20% relative. This characterization technique should allow chemical characterization of faceted particles to be more accurate because the x-ray and absorption path lengths can be directly measured and modeled.

Future Plans: The initial testing and development of this approach has been done on pigment particle in the size range of 200 x 500 nm. Plans include testing on smaller particles in the nanoparticle range. Additionally, we plan to collect data from other techniques to acquire thickness and surface morphology information to combine with faceting models developed with this approach.

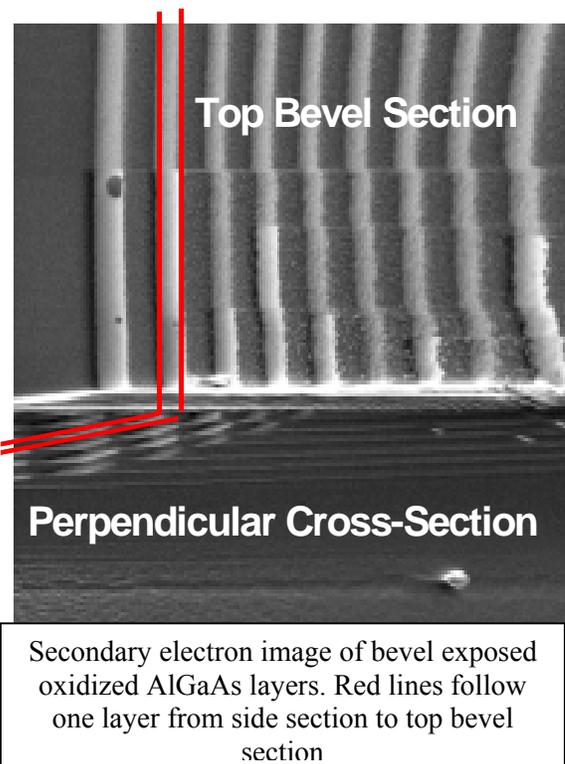
Bevel Craters For Surface Analysis Of AlGaAs/GaAs Multi-layer Structures

CSTL Program: Microelectronics

Authors: *S. Wight, G. Gillen, and A. Fahey*

Abstract: The lateral wet-thermal oxidation of high aluminum content AlGaAs layers can be used to form buried oxide layers that are widely employed for the fabrication of vertical cavity surface emitting laser structures used in the optoelectronics industry for fiber optic data links, proximity sensors, encoders, laser range finders, laser printing, bar code scanning, and optical storage. The challenge is to analyze the variation in composition of the oxidized layers laterally and as a function of depth. The oxidized portions of the AlGaAs layers ion beam etch much more slowly than the un-oxidized AlGaAs and the interstitial GaAs layers. This complicates depth profile measurements by Auger or secondary ion mass spectrometry (SIMS). A commercial SIMS instrument was modified to produce a variable dose ion beam raster that etches a bevel ramp crater into a surface to reveal subsurface structure. The raster profile, ion species and ion energy were evaluated by scanning electron microscopy and Auger imaging in a commercial UHV Auger microscope. Oxygen was chosen over cesium and gallium as the primary ion species because of the decrease in differential sputtering. The lower energy (3 keV) oxygen was selected over higher energies because it reduced surface roughening. Low energy Argon (1 keV) ion sputter cleaning is being used in the Auger microscope to remove the primary sputter ion species because oxygen is an important component in the elemental analysis.

Purpose: The lateral wet-thermal oxidation of high aluminum content AlGaAs layers can be used to form buried oxide layers that are widely employed for the fabrication of vertical cavity surface emitting laser structures. The challenge is to analyze the variation in composition of the oxidized layers laterally and as a function of depth. The oxidized portions of the AlGaAs layers ion beam etch much slower than the un-oxidized AlGaAs and the interstitial GaAs layers. This complicates depth profile measurements by Auger or secondary ion mass spectrometry (SIMS). A commercial secondary ion mass spectrometer (SIMS) instrument was modified with a custom external raster waveform. This waveform was designed to deliver a variable ion dose. The desired result was a bevel crater, one that ramps down from the top surface at one edge to some depth at the other edge. This produces lateral magnification of the subsurface structure for



analysis by static SIMS or scanning Auger spectroscopy. The diagonal slice through the AlGaAs/GaAs multi-layers exposes a larger portion of the oxidized AlGaAs layer for subsequent analysis.

Major Accomplishments: Initially a Cs^+ primary ion beam was used to etch bevel craters because oxygen content was of interest, but it created excessive roughness. Crater wall analysis revealed that the oxidized AlGaAs etched more slowly than the surrounding materials. These problems were not present in a bevel of the un-oxidized multi-layer. An O^+ beam was applied to bevel crater production and it was discovered that the lower energy 3 keV beam was better suited because of decreased differential sputtering and roughness. A focused ion Ga^+ beam was attempted for bevel crater production to get away from the problem of leaving oxygen on the surface because it is of interest in the analysis. Gallium failed for the same reasons as the cesium, but the low energy (1keV) Ar^+ ion gun in the Auger instrument was successful in removing the implanted oxygen from the bevel crater production.

Impact: The development of the bevel crater has facilitated the analysis of the oxidized AlGaAs. The bevel crater technique has also been successfully applied to other multi-layer structures, such as Ni/Cr depth profile standard and KRIS sample.

Future Plans: The bevel approach could also be applied to other buried structures such as gates and CMOS contaminants and complex device stacks. The use of low energy ion sputtering to remove the primary ion species and induced damage will be further studied to maximize the readiness of the bevel surface for further analyses. Use of a reactive ion species other than oxygen, SF_5^+ for example may also prove productive.

Autoradiography Measurements to Quantity Activity of Co-60 Particles

CSTL Program: Forensics and Homeland Security

Authors: *C.J. Zeissler (837); and R.M. Lindstrom (839)*

Abstract: An autoradiography measurement approach is being developed to support forensic analysis on dirty bomb debris at a level that falls over one order of magnitude below conventional detection capabilities. The physical nature of particulate matter presents special measurement challenges. For instance, conventional biological standards cannot be utilized. Standards for biology consist of a limited list of radiotracers in thick, tissue slices or gene separation gels. Particles, however, act as point sources, whose positional geometry can significantly influence the measurements. Another challenge is that the activity of particles in environmental dusts cannot be adjusted as one might in biological tracer studies, meaning that special treatment has to be given to signal-to-noise problems. This year we studied the fading characteristics of two phosphor detectors, measurement variability, phosphor calibration, spatial resolution, Co-60 detectability, and ease of adoption. Eventually we plan to produce working standards and a measurement protocol for potential use by national forensic authorities.

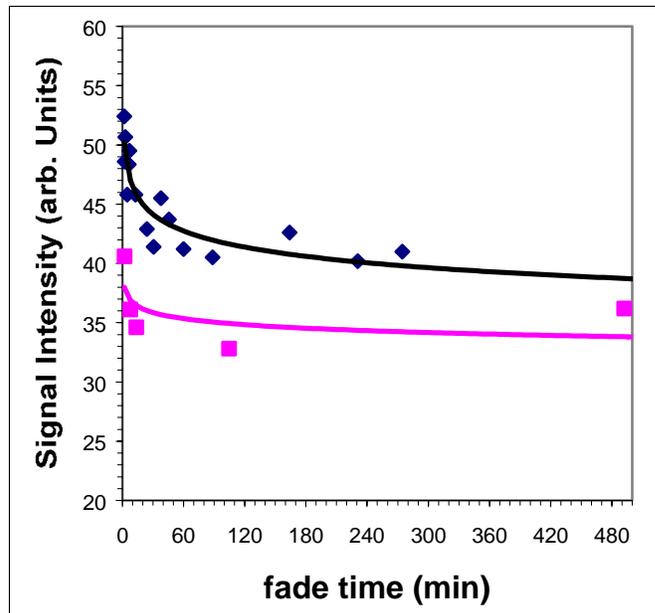


Fig. 1. Fading curves for two autoradiography phosphor detectors using a 3 Bq Co-60 source.

Purpose: The purpose of this research into autoradiography measurements is to develop a quantitative, nondestructive and discrete measurement capability for particles that emit beta radiation at or below mBq levels. Single particle detection and characterization measurements of a particle population are applicable to forensic dirty bomb investigations. Dirty bomb debris may include beta-emitting particles of Co-60, Cs-137, Sr-90, etc. Individual particle analysis enables the collection of a variety of discrete

chemical, isotopic, and microstructural data on each particle in a population. This data may be used to deconvolve sources and histories. In contrast, information obtained from conventional methods such as gamma spectrometry or radiochemistry provides a measurement averaged over the whole sample, and does not provide additional forensic information available in the microstructure or morphology of each particle.

Major Accomplishments: The digital autoradiography method has been shown to detect Co-60 nondestructively at a level at least one order of magnitude below low-background gamma spectrometry methods. Calibration down to 10 mBq has been achieved. Detection down to about 1 mBq or lower appears to be possible, but has not been verified at this stage of the project. Measurement uncertainty that is not due to counting statistics is approximately 10%. The difference in spatial resolution between two different detectors has been evaluated.

Impact: A nondestructive, sensitive characterization method that preserves discrete particle information can have great forensic utility. Conventional methods should continue to be sufficient for conventional detection and characterization, but they have limited sensitivity and forensic value. With this new microcharacterization method, previously undetectable debris on dirty bombs or residues from alleged manufacturing locations could be used towards the identification of terrorist activities. Ultimately, such information can be used to prevent future manufacture or deployment of dirty bomb devices.

Future Plans: Fading and sensitivity measurements will be continued. Working standards will be created by neutron-irradiation of microscopic cobalt particles. The effect of particle geometry will be investigated using working standards and preexisting Co-bearing metal flakes and oxide agglomerates. Calibration below 10 mBq will be pursued. The characterization of the particles will include isotopic, chemical, and morphologic analysis. The ease of adding the isotopic, chemical and morphologic measurements to the easier-derived radioactivity measurements will be considered relative to practical application.

The NIST-EPA Interagency Agreement to Develop Metrology Supporting PM_{2.5} Research: Status and Completion of Selected Tasks

CSTL Program: Environmental Technologies and Services

Authors: *M. Verkouteren, G. Klouda, J. Conny, R. Fletcher, J. Small, L. King, and E. Steel; C. Presser (836); R. Zweidinger, and G. Norris (EPA)*

Abstract: Through the *Standard Materials for the PM 2.5 National Research Program*, interagency agreement DW13939042-01-0 between NIST and the US EPA, CSTL initiated several activities directed at the development of needed methods and standard materials for the accurate chemical analysis of particulate matter. Activities included: (a) production of a filter-based urban dust standard material; (b) investigation of methods for certifying black carbon; and (c) production of glass thin-film prototype standards on PTFE for XRF analysis of sulfur. These activities were designed to address the significant uncertainties inherent in chemical analysis of PM_{2.5}, which limits the usefulness of PM_{2.5} data in health studies and receptor modeling, as well as in studies investigating the PM_{2.5} link with global climate change.

Purpose: To provide fundamental chemical metrology and SRMs needed by the measurement communities involved in the national Particulate Matter (PM) research program.

Impact: Evidence is accumulating that black carbon in PM_{2.5} adversely affects human health, being implicated in diseases from asthma to cardiovascular problems, and according to new modeling efforts, black carbon in PM_{2.5} exerts a large warming influence on global climate. The lack of PM standard materials, especially for black carbon, has contributed to uncertainties about this pollutant's sources, its chemical and physical properties, and its radiative properties in the atmosphere.

Future Plans: We will finish SRM Project 2784 early in FY03. We also intend to continue the engineered soot project, where we hope to produce PM containing soot that closely represents PM found in the environment. Microanalytical methods will be developed to enable the visualization of the engineered particle populations. We also plan to monitor the long-term stability of the prototype glass thin-films, especially regarding their sulfur content and cohesion to PTFE.